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Environmental Monitoring Reference Manual for Synthetic Fuels Facilities

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ENVIRONMENTAL MONITORING REFERENCE MANUAL FOR SYNTHETIC FUELS FACILITIES

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16. ABSTRACT

The manual is intended as a technical aid to applicants, the U.S. Synthetic Fuels Corporation (SFC), and environmental reviewers in developing and reviewing plans covering source and ambient monitoring around coal-, oil shale-, and tar sand-based synfuels plants, consistent with the Energy Security Act. The Act, which established the SFC, specifies that applicants for SFC financial assistance must develop an acceptable plan for environmental monitoring of the construction and operation of the proposed synthetic fuels facilities, following consultation with the EPA and other agencies. The manual does not provide rigorous specifications for an acceptable monitoring plan. Rather, it describes approaches to consider and issues to address in developing a monitoring plan (or an outline of a plan). The exact content of the plan or outline for a specific facility would depend on conditions associated with that plant.

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a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
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Fossil Fuels	Stationary Sources	21D
Monitors	Synthetic Fuels	14G
Coal		08G
Oil Shale		
Bituminous Sands		

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This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

In preparing this manual, the Environmental Protection Agency has consulted with the U.S. Synthetic Fuels Corporation. Release of the manual does not reflect its endorsement by the Corporation.

NOTICE

This manual will be revised if necessary based upon initial experience with its use in the development and review of environmental monitoring plans and plan outlines. Comments for consideration in any such revisions of the manual should be provided by October 31, 1983, to:

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Foreword

This Environmental Monitoring Reference Manual for Synthetic Fuels Facilities is intended to aid applicants to the Synthetic Fuels Corporation (SFC)--and to aid other developers of synthetic fuels plants--in developing Environmental Monitoring Plans (and outlines of such plans) covering source and ambient monitoring. The manual is also intended to assist Federal and State agencies in reviewing these monitoring plans and plan outlines. This manual is provided as one component of the Agency's input to the consultation process specified in Section 131(e) of the Energy Security Act.

This manual is not intended to provide rigorous specifications for an "acceptable" monitoring plan. The ultimate acceptability of a plan is determined by the SFC. Nor is the manual intended as a comprehensive definition of the compliance monitoring that will be required by permits. Rather, the manual describes approaches that can be considered, and issues that need to be addressed, in the development of a monitoring plan or outline for a synthetic fuels plant. The exact content of the monitoring plan or outline for any specific facility would have to be developed taking into consideration the particular circumstances associated with that plant.

As developers and reviewers of monitoring plans and outlines begin to use this manual, potential improvements in the content or format might become apparent which would enable the manual to better achieve its intended purpose. If the Agency receives substantive comments from initial users, the manual will be revised as appropriate.

Users of the manual are therefore encouraged to submit--by October 31, 1983--any comments that they feel should be considered in the revision of this document. Comments should be directed to:

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Industrial Environmental Research Laboratory (MD-61)
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Donald J. Ehreth, ~~Acting~~ Director
Office of Environmental Engineering
and Technology

Abstract

The Energy Security Act, which establishes the Synthetic Fuels Corporation (SFC), specifies that applicants for SFC financial assistance must develop a plan, acceptable to the Board of Directors, for the monitoring of environmental and health-related emissions from the construction and operation of the synthetic fuel project, following consultation with EPA and other agencies. The SFC has published interim Environmental Monitoring Plan Guidelines outlining SFC policy for preparation of the required monitoring plans. This Environmental Monitoring Reference Manual is intended as a technical aid to the applicants and to reviewers in developing and reviewing the environmental monitoring plans for coal-, oil shale- and tar sand-based synthetic fuel plants, consistent with the Act and the SFC guidelines. It also should be useful for plants processing peat and heavy oil. The manual considers source and ambient monitoring; it does not address industrial hygiene, wildlife, water consumption or socioeconomic monitoring.

This manual outlines some features which could be considered in developing an environmental monitoring plan (or monitoring plan outline). These features include approaches for selecting discharge streams and ambient media to be monitored, substances/survey procedures to be addressed in the various streams and media, sampling and monitoring techniques, and monitoring frequencies. A phased approach is emphasized, in which an initial comprehensive "survey" (Phase 1) monitoring phase identifies the species which should be addressed in a subsequent reduced extended-term (Phase 2) monitoring program. The manual addresses both regulated and unregulated substances. Nothing in the manual supercedes compliance-required monitoring.

This reference manual is not intended to provide specifications for an "acceptable" monitoring plan. The exact content of the monitoring plan for any specific synfuels plant would have to be developed, in consultation with agencies specified in the Energy Security Act, for application to the particular conditions associated with that plant. However, the manual does describe practical approaches to consider in developing an effective monitoring plan (or plan outline) tailored to the needs of a specific facility.

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SECTION 1

INTRODUCTION

1.1 PURPOSE

The purpose of this reference manual is to aid applicants to the U.S. Synthetic Fuels Corporation (SFC) and other synthetic fuels plant developers in preparing environmental monitoring plans (and outlines of such plans) covering source and ambient monitoring for coal-, oil shale-, and tar sands-based synthetic fuels facilities. The manual is also intended to assist Federal and State agencies in reviewing these monitoring outlines and plans. The manual is provided as one component of the Environmental Protection Agency (EPA) consultation process in monitoring plan development, as specified in Section 131(e) of the Energy Security Act.

This manual is not intended to provide specifications for an "acceptable" monitoring plan. The ultimate acceptability of a plan is determined by the SFC. Rather, the manual describes approaches to consider and issues to address in developing a plan or outline. The exact content of the monitoring plan or outline for any specific facility would need to be tailored to meet conditions associated with that particular plant.

1.2 BACKGROUND

The Energy Security Act of 1980 (PL 96-294)--which establishes the SFC--includes the following requirement (Section 131(e) of the Act):

> "Any contract for financial assistance shall require the development of a plan acceptable to the Board of Directors (of the SFC), for the monitoring of environmental and health-related emissions from the construction and operation of the synthetic fuel project. Such plan shall be developed by the recipient of financial assistance after consultation with the Administrator of the Environmental Protection Agency, with the Secretary of Energy, and appropriate State agencies."

The intent of Congress concerning Section 131(e) is discussed in the Joint Explanatory Statement, Committee of Conference for this Act:

> "The monitoring of emissions--gaseous, liquid or solid--and the examination of waste problems, worker health issues and other research efforts associated with any synthetic fuel project receiving assistance pursuant to this Part will help to characterize and identify areas of concern and develop an information base for the mitigation of problems associated with the replication of synthetic fuel projects."

In implementing Section 131(e), the SFC is using a two-stage approach in which an applicant (1) develops an outline of the monitoring plan for incorporation into the financial assistance contract, and (2) develops the monitoring plan itself, based on the outline, after the financial assistance contract is executed. The SFC has published interim Environmental Monitoring Plan Guidelines (April 1, 1983), setting forth the procedural steps and the broad substantive areas to be addressed in developing outlines and plans. (See Appendix I.) These interim Guidelines are subject to public comment; final Guidelines will be prepared by SFC following receipt of public comments.

This manual is intended to serve as one component of the mandated consultation process for monitoring plan development. Another component envisioned in the process is direct contact between EPA and the applicants, in which EPA assists them in applying the manual to the specific circumstances of each proposed facility. The manual is designed to aid in the development and review of both the outlines and the monitoring plans, consistent with the intent of Section 131(e) and current SFC monitoring guidelines.

1.3 SCOPE AND CONTENT

The scope of the monitoring guidance is defined by the following topics.

Coal-, oil shale-, and tar sands-based synthetic fuels processes - These processes include coal gasification (high-, medium-, and low-Btu), coal liquefaction (indirect and direct), oil shale mining and retorting, and tar sands processing. In general, the manual also should apply to monitoring heavy oil, peat and other synfuels processes.

Source monitoring and ambient monitoring - Source monitoring includes chemical and biological analyses on discharge streams (gaseous, aqueous, solids) including fugitive discharges inside the plant boundaries. Source monitoring also includes monitoring environmental control device performance. Ambient monitoring includes chemical and biological tests on the unconfined environment in the vicinity of the synfuels plant (atmosphere, surface waters, water in the unsaturated soil, surface aquifers, deep aquifers and the soil). It is envisioned that source and ambient monitoring programs will be integrated. The manual does not address industrial hygiene, wildlife, water consumption, or socioeconomic monitoring.

Regulated and unregulated substances - The intent of the monitoring is to develop a synfuels data base on environmental and health-related emissions that will aid in mitigating problems in future technology replications. Therefore, the monitoring should not be limited to the substances for which regulations or standards already exist (either in related industries or the ambient environment). Many substances which might be discharged from synfuels plants are not currently regulated. Accordingly, the monitoring approaches considered in this manual address unregulated substances as well as regulated pollutants. This consideration of unregulated substances is consistent with the provisions of the SFC monitoring plan guidelines.

Pre-construction, construction, and operational monitoring - Source monitoring addresses monitoring only during plant operation, while ambient monitoring is expected to occur during all three periods.

Monitoring Control Device Performance - As one component of source monitoring, control device monitoring could address both the inlet and outlet streams of a control device as well as suitably selected operating parameters. The performance/reliability of conventional control techniques in synfuels plant applications has not been demonstrated in many cases. An improved understanding of control device performance, obtained by monitoring on initial synfuels plants, could help mitigate environmental problems in future replication of synfuels plants.

The manual provides the following information to aid in developing monitoring plans and outlines.

Suggested Data Base Content - The manual presents in some detail a suggested reasonable content for the "information base" referred to in the Congressional explanatory statement. The manual suggests which substances might be analyzed in the various types of discharge streams in order to establish a sound information base. The analyses for this data base include both (1) analyses for specific compounds, and (2) the use of survey analytical techniques to screen for classes of compounds in streams where specific components cannot be predicted a priori. The data base analyses include biological and physical property tests as well as analyses for chemical components.

The data base suggestions were derived by considering substances currently regulated in related industries and the ambient environment; substances for which monitoring is typically specified in environmental permits for related industries; unregulated substances which have been observed in existing source test data from synfuels facilities; and unregulated substances which are included in various recognized pollutant lists and which might reasonably be expected to be discharged from a synfuels plant. The data base includes suggestions concerning which specific substances/survey techniques/ bioassays might reasonably be considered in which streams (source monitoring) or which ambient media (ambient monitoring) under different circumstances. These considerations are addressed in Section 4.1 (source) and Section 5.1 and Appendix C (ambient).

Alternative Approaches to Monitoring - Several alternative approaches to developing the data base are presented. Most involve a phased monitoring program in which a fairly comprehensive survey is done in the first phase followed by a reduced second phase based on first-phase results. The monitoring frequency and duration for each phase can be based on site-specific statistical considerations as described in Sections 4.2 and 4.3 (source) and Section 5.2 (ambient).

Sampling, Sample Handling, and Analysis - Alternative monitoring procedures are presented which can be considered for each substance to be analyzed or each class of chemicals to be analyzed by a survey technique. Capabilities of and estimated cost ranges for individual procedures are indicated in Section 4.4 and Appendix A (source), and Section 5.3 and Appendices D through H (ambient).

Quality Assurance/Quality Control - Suggestions for a meaningful quality assurance/quality control program are also given in Sections 3.0 and 4.2.1.3 and the appendices describing monitoring procedures.

1.4 USE OF MANUAL

This manual does not provide specifications for an "acceptable" monitoring plan. Nothing in the manual constitutes a "requirement". The manual is intended only to describe alternative approaches that can be considered in developing the data base referred to in the Congressional explanation. These alternatives can be considered in structuring a monitoring plan (or plan outline) tailored to the needs of a specific facility.

The suggestions in this manual will in no way alter permit monitoring requirements for a specific facility, nor relieve a facility from complying with permit monitoring obligations. As a practical matter, most of the compliance monitoring required by permits for a particular facility will generally be included in this manual. However, the monitoring approaches described in the manual do not necessarily include, nor are they necessarily consistent with, every conceivable set of permit requirements that might be encountered in practice. These requirements will be established by the cognizant permitting agency based on the conditions at a specific site.

The interim SFC monitoring plan guidelines specify the content of monitoring plan outlines and of monitoring plans themselves. According to these guidelines, the outline should include:

- a summary of compliance monitoring obligations,
- the regulated and unregulated substances to be monitored (or, where specific unregulated substances cannot be identified beforehand, an indication of the classes of substances that will be addressed),
- the general location of the monitoring (i.e., stream or ambient medium),
- how the monitoring generally would be performed e.g., high-volume sampler (where specific unregulated substances cannot be identified beforehand, the methods by which substances will be identified should be given),
- the duration of monitoring, and
- background information on the synfuels project to enable review of the outline (e.g., overall process description, process block flow diagram, control system specifications, plot plans, detailed site description, supporting environmental data, etc.).

The monitoring plan should include:

- any necessary further definition of the substances to be monitored;
- detailed monitoring site locations;
- specific sampling/sample handling/analytical protocols, including equipment and methods;
- monitoring frequency for each substance at each monitoring location; and
- background information, as described for the outline above.

This reference manual can be used to fulfill the above specifications for monitoring plans and outlines for a specific plant by following the steps listed below:

1. Identify discharges and ambient media of concern - Review the plant design drawings and flowsheet and the detailed site plan to identify discharge streams (and controls) and ambient media of interest. These are the streams/media to be sampled in the monitoring program.

2. Classify the discharge steams - For source monitoring, classify the streams of concern using the generic stream categories defined in Tables 4-1, 4-2, and 4-3 (Section 4.1) for gases, liquids, and solids, respectively. The stream categories are logical and easy to understand. Category assignments will be based on the following:

   --Is the discharge a gas, liquid, or solid/sludge?

   --Does the discharge contain organics? (is it organic-rich or organic-lean?).

   --Is the discharge unique to synthetic fuel processing (e.g. waste from raw reactor effluent cooling water treatment), or non-unique (e.g. flue gas from coal-fired boiler)?

3. Select substances to be analyzed - Use Tables 4-4 through 4-6 (gaseous, aqueous/liquid, and solid discharges) in Section 4.1.2 to select the specific substances to be analyzed in samples from each discharge stream (or to select the chemical classes of unregulated substances to be analyzed using survey

analytical techniques if specific substances cannot be defined beforehand). The same tables plus Appendix C can be used to select substances to be monitored in ambient media.

The information in Tables 4-4 through 4-6, which are organized by generic stream category, must be tailored to a specific plant. The information needed to make plant-specific selections for monitoring includes:

--engineering assessment of expected compositions of discharges from the plant,

--site- or process-specific test data on discharges and their composition, and

--permit requirements.

4. Prepare a Test Matrix - Based on the selections made in 1 and 3 above, prepare a matrix of the streams (i.e., the source monitoring locations) and ambient media to be sampled, the species/classes to be analyzed in each, and the process data required to interpret the monitoring data and define operating conditions at the time of sampling.

5. Select Ambient Monitoring Locations - Use the comments in Section 5.1.2 as a guide in the site-selection process for ambient monitoring stations.

6. Select Sampling, Sample Handling, and Analysis Methods - Refer to Section 4.4 and Appendix A (source) and to Section 5.3 and Appendices D through H (ambient) as a guide in selecting sampling, sample handling, and analysis methods for each species or class of chemicals in each stream or ambient medium. Select potential source monitoring procedures for each substance from the alternatives in Tables 4-27 through 4-29.

(Survey techniques used in screening for chemical classes when specific substances cannot be defined beforehand are given in Tables 4-24 through 4-26).

Find the descriptions of the candidate procedures in Appendix A. The applications, limitations, and estimated costs are discussed there for each procedure, and references are given. An experienced analyst will be able to select suitable techniques for a specific plant from the alternatives by taking the following site-specific factors into account:

- --the analytical sensitivity needed for a component in a specific stream,
- --the potential presence of interfering species, and
- --the available analytical facilities and equipment.

Follow the same process for ambient monitoring procedures, using the information in Appendices D through H.

The level of detail in the appendices and tables provides a general description of alternative techniques, which is adequate for preparing the monitoring plan outline. However, in some cases--in particular, for complex organics--the description in the manual might not be adequate to define the specific sampling/sample handling/analytical procedures in the detail required for the monitoring plan. In these cases, an experienced analyst will need to define the details (especially sample handling/preparation techniques and sample size considerations). The references given for each method should be consulted for details.

7. Define Phased Monitoring Approach - The monitoring approach that is chosen will influence the selection of monitoring frequency and duration. The monitoring approach emphasized in

Section 4.2 employs the concept of phasing. Phase 1 includes monitoring needed initially to define a baseline data base and is of limited duration. Phase 2 is based on first-phase results and involves a reduced monitoring effort for the remainder of the plant operating life to track the Phase 1 data base using "indicator" species to identify deviations from the baseline data. Two other possible approaches-- one involving a different method of phasing and one not involving phasing-- are described in Section 4.3. The user can adopt one of these approaches or suggest an alternative. If an alternative approach is suggested, its impact on the resulting data base should be evaluated carefully.

8. Select Monitoring Frequency and Duration - If the monitoring approach in Section 4.2 is employed, use the practical and statistical guidance in Sections 4.2.1.2 and 4.2.2.2 to select monitoring frequency (for the plan) and duration (for the outline and plan). If a different approach is used, considerations similar to those in Sections 4.2.1.2 and 4.2.2.2 can be used to select frequency and duration.

   Applying the statistical principles requires establishing certain decision criteria (e.g., desired accuracy). The manual describes the types of statistical decisions and the impacts on sampling frequency and duration of monitoring. A tradeoff between improved statistical accuracy (increased data quantity) and reduced sampling frequency/duration (lower cost) must be considered in selecting frequency and duration for the site-specific monitoring plan.

The interim SFC monitoring guidelines specify that outlines and monitoring plans should also address quality assurance/quality control (QA/QC) measures and data management and reporting procedures. QA/QC is discussed in Section 3 of this manual. Data management and reporting are not specifically addressed in this manual (except in terms of statistical evaluation and Phase 2 design); EPA suggestions concerning data management/reporting will be addressed separately.

The interim SFC monitoring guidelines specify formation of a Monitoring Review Committee comprised of representatives from the developers, the consulting agencies and the SFC. This committee will review the monitoring results and advise the SFC about any significant results and any resulting adjustments in the monitoring program that might be warranted. If a phased monitoring approach is used--wherein a reduced, second-phase program is designed based on results from the first phase--the Monitoring Review Committee could be involved in helping direct the Phase 2 design.

1.5 OTHER REFERENCES

In conducting a source and ambient monitoring program of the type outlined in this manual, information from a large number of references might be applicable. Key references are included at the end of each section and appendix.

In addition to this monitoring reference manual, the EPA-ORD synthetic fuels program has generated another series of documents, the Pollution Control Technical Manuals (PCTMs), which can be used in evaluating discharges and control technologies for synthetic fuels facilities. Based on publicly available information, the PCTMs estimate the compositions of the various waste streams (prior to control), and describe alternative control techniques that might be considered for application to each waste stream. PCTMs have been prepared for the following synfuels technologies:

Lurgi-Based Indirect Coal Liquefaction and SNG (Report No. EPA-600/8-83-006) - NTIS Accession No. PB83 - 214478

Koppers-Totzek-Based Indirect Coal Liquefaction (Report No. EPA-600/8-83-008) - NTIS Accession No. PB83 - 214502

Exxon Donor Solvent Direct Coal Liquefaction (Report No. EPA-600/8-83-007) - NTIS Accession No. PB83 - 214486

Lurgi Oil Shale Retorting with Open Pit Mining (Report No. EPA-600/8-83-005) - NTIS Accession No. PB83 - 200204

Modified In-Situ Oil Shale Retorting Combined with Lurgi Surface Retorting (Report No. EPA-600/8-83-004) - NTIS Accession No. PB83 - 200121

TOSCO II Oil Shale Retorting with Underground Mining (Report No. EPA-600/8-83-003) - NTIS Accession No. PB83 - 200212

Control Technology Appendices for Pollution Control Technical Manuals (Report No. EPA-600/8-83-009) - NTIS Accession No. PB 83-214734.

These PCTMs are available from the National Technical Information Service (NTIS), 5285 Port Royal Road, Springfield, Virginia 22151.

SECTION 2

MONITORING CONCEPTS

2.1 APPROACH TO MONITORING

The stated purpose of the Section 131(e) monitoring--to develop a data base which can be used to identify environmental problems--suggests the need for a fairly broad monitoring program. A monitoring approach must be selected which will allow this broad data base to be developed in a realistic and cost-effective way.

Synthetic fuels processes could produce and potentially discharge a wide array of organic compounds and any trace metals present in the feedstock. While source tests have been conducted on the discharges from some synfuels facilities (including pilot plants and a few small commercial units), these data are not necessarily representative of large, commercial-scale plants. In most cases, certain discharge streams that would be present in a commercial facility were missing. And some of the streams present were not representative either because the facility was not a complete, integrated plant, or because the plant was not designed, operated, or controlled in a manner representative of a modern commerical facility. Nevertheless, these data still suggest which classes of compounds might be present in discharges from a large commercial facility. They cannot however, be used as a rigorous indicator of all substances that will be present or of substances that will always be present in commercial discharge streams. Thus, the design of a monitoring program that must develop a broad data base is complicated because a wide range of substances might be present, and there is only a general (class) indication of what the actual substances might be.

A monitoring approach that addresses these concerns by monitoring specifically for every potential substance that might be present would not be cost-effective. On the other hand, a monitoring approach that monitored only for a limited, preselected list of substances could overlook some important substances. And even after the substances present have been identified, the number of substances might be so large that extended monitoring for all of the substances could become expensive.

To overcome these potential difficulties, this manual presents the following considerations:

- Where the specific (unregulated) substances cannot be identified beforehand, survey analytical procedures could be employed during initial monitoring to screen for the substances which are actually present.
- The monitoring program could be phased so that the results of the above-mentioned screening in the first phase could be used to design a reduced second phase effort. The second phase could be designed to monitor for fewer substances than were actually observed during Phase 1.

Three alternative monitoring approaches are discussed in this manual, all of which involve the use of survey analytical techniques, and two of which involve phasing. The designer of a monitoring plan/outline for a given plant might identify additional approaches, beyond these three, suitable for that plant. The substances to be monitored, monitoring location, monitoring frequency and duration, which must be specified in the monitoring plan and outline, would be determined by the overall monitoring approach. The choice of monitoring techniques can also be influenced by the overall approach, if survey analytical procedures are called for. No matter what overall approach is selected, monitoring for any regulated substances would continue as required by permits.

The three alternative approaches discussed in this manual are summarized below. These approaches are described in more detail in Sections 4.2 and 4.3. If a different approach is proposed in the monitoring plan for a specific plant, the plan should consider how the results from the new approach would compare with those from the approaches discussed here.

Phased approach using indicators in Phase 2. Phase 1 monitoring would include: survey analytical procedures to screen for (unregulated) chemical substances in selected classes when the substances cannot be defined beforehand; specific component analyses for substances of interest that can be identified beforehand; and biological tests. These Phase 1 data would be collected over an initial period of steady state plant operation and would define the "baseline" data base. These Phase 1 data would be statistically evaluated to select particular substances, or parameters (such as COD), which might serve as "indicators" for the other substances/parameters observed during Phase 1. Monitoring during Phase 2 would then proceed, addressing only the indicators. In theory, the entire baseline data base could thus be tracked during Phase 2 by monitoring certain indicators. Phase 1 measurements (for the substances represented by a given indicator in a given stream) would be repeated if an excursion (of some pre-defined magnitude) in that indicator suggests that the baseline has shifted. The extended monitoring during Phase 2 would provide the data history needed for extrapolation of results in replication of synfuels technology. The frequency/duration of monitoring during Phases 1 and 2 would be determined by the desired accuracy of the results, including the accuracy of detecting baseline shifts during Phase 2. The advantages of this approach are: 1) the use of survey analytical techniques avoids the need to guess which substances will be present; 2) the use of phasing allows a significant reduction in the monitoring effort after the first phase and still provides a broad baseline; and 3) the use of indicators allows tracking "baseline" data throughout Phase 2, and eliminates the need to decide which of the substances observed in Phase 1 warrant continued monitoring. One concern with this approach is the ability to define a suitable relationship between potential indicators and represented substances based on the Phase 1 results.

Phased approach with deletions following Phase 1. In this approach, Phase 1 would proceed exactly as described above, during the initial period of steady state operation. However, the Phase 1 results would be interpreted differently. Rather than using Phase 1 results to select indicators, the results would be used to define which of the observed Phase 1 substances should continue to be monitored during Phase 2, and which should not. Phase 2 would then address only those substances which were both a) observed during Phase 1, and b) judged to be significant enough to warrant extended monitoring. This approach offers the benefits of survey procedures and phasing, as does the previous approach, and avoids the potential difficulties inherent in trying to develop statistical relationships between indicators and represented substances. However, this approach would require the sometimes-difficult decision about which substances warrant continued monitoring. Nor does this approach assure that Phase 2 will represent the entire Phase 1 data base.

Non-phased approach. In the non-phased approach, monitoring for the entire data base (everything in Phase 1) would be continued with no effort to reduce the monitoring as results become available. This approach would offer the benefits of the survey analytical procedures, as in the approaches above, and would avoid the difficulties involved in designing a Phase 2 program. However, this approach would not provide the advantage of potential reductions/cost savings from a reduced Phase 2. This approach would produce the most comprehensive data set because Phase 1 monitoring for the total data base would continue in place of the reduced Phase 2. Therefore, it might be desirable to select a total duration for the non-phased program which would be shorter than for the phased approaches.

The phased approaches involve data interpretation and decisions regarding the Phase 2 content at the end of Phase 1. The Monitoring Review Committee--described in the interim SFC monitoring guidelines as an advisor to the SFC in reviewing the monitoring data--could help direct the Phase 2 design activity.

2.2 INTEGRATION OF SOURCE AND AMBIENT MONITORING

Source and ambient monitoring are two complementary components of an integrated monitoring program. Source monitoring identifies the substances discharged to the environment. Ambient monitoring indicates where these substances actually appear/accumulate and suggests the transformations the substances might experience in the environment. One element of the review and interpretation of monitoring data should be comparison of the source and ambient results.

In this manual, it is assumed that the source and ambient monitoring programs use the same approach--i.e., including survey analytical techniques and perhaps phasing. Employing similar broad survey approaches in both programs should help to identify the relationships between source and ambient results. As a practical matter, the results from source monitoring can be used to alert the operators of the ambient program about the types of substances or transformed substances that might be present. Conversely, excursions in the ambient results should alert source monitoring operators to look for the substances of concern in the pertinent discharges. This integration will be of particular importance during Phase 2, when monitoring might be reduced and the risk of failure to detect substances increases. Continued inconsistencies between the source and ambient results that cannot be explained should be investigated.

SECTION 3

QUALITY ASSURANCE

A well planned and executed Quality Assurance (QA) program is necessary for the successful completion of any monitoring program. Monitoring efforts are expended needlessly if the data obtained are of poor or unknown quality. Normally, the quality of data is expressed in terms of five parameters: precision, accuracy, completeness, representativeness, and comparability. The quality of data is affected by nearly every step in setting up and implementing a monitoring program, from planning and executing the program to maintaining data archives and analyzing the data.

An SFC applicant should note the principles of EPA's quality assurance program. Under the EPA program, the absolute quality requirements for each data set are not specified. It is the responsibility of the project personnel to set reasonable goals. However, the EPA does insist that the quality of the data be known and well documented. This point is particularly relevant to many of the pollutants associated with the synfuels industry for which quality assurance procedures have not been standardized or widely accepted. Under the EPA quality assurance program, the quality of data obtained from all sampling and measurement protocols must be known and documented, regardless of how recently the procedures have been developed. The fundamental question asked of a project monitoring director is "What makes you think your data are reliable?" and "How reliable are they?". These questions are germane, no matter how new or experimental the sampling or measurement protocol.

The essential elements which should be included within a quality assurance project plan are discussed in detail in the interim guidelines document available from EPA's Quality Assurance Management Staff, Office of Research and Development (3-1).

Broadly, quality control (QC) has to do with making quality what it should be, and quality assurance has to do with making sure that quality control is what it should be. More precisely, quality control aims at providing a quality of data, product or service that meets the needs of the users in terms of adequacy, dependability and economy. The quality control system integrates the quality aspects of the specifications of what is desired, the production to meet the specifications, the inspection to determine if the specifications were met and the review of usage for revision of specifications. The quality assurance program aims at providing assurance that the overall quality control system is implemented effectively. Quality assurance requires an evaluation of the completeness and effectiveness of the quality control and initiation of corrective measures if necessary. Quality assurance programs, therefore, involve audits, verifications and evaluation of quality factors for specification, production, inspection and utilization (3-2).

A quality assurance plan should be developed, approved and implemented for each synthetic fuel plant monitoring program. The plan should be based on four fundamental principles: (1) responsibility for quality assurance must extend to all levels of management; (2) the specification of the quality of data must be explicit, i.e., how good does the data have to be for the purposes of the project; (3) the program must have adequate steps to assure that data of the needed quality are obtained; (4) implementable and effective corrective actions must be taken when the data are of unacceptable quality. Good statistical design of the sampling plan is of utmost importance. The quality assurance plan must address all of the activities which occur during monitoring including sampling, analysis, data reduction, and data interpretation. The plan must also define a QA structure and the capabilities required for QA and data management personnel.

3.1 ORGANIZATION OF QA/QC

The quality assurance and quality control functions should be organized to insure the generation of reliable and consistent analytical data to permit the data interpretation required for plant monitoring. The Quality Assurance/

Quality Control (QA/QC) activities should be coordinated for consistent review of the development and implementation of the specific quality control activities for sampling, organic analysis, inorganic analysis, and data management.

Specific QC protocols should be developed for the sampling program and for each of the major analytical areas. Training sessions and scheduled QC activities should be conducted. Reporting and record-keeping should be defined explicity, and QC data analysis documented. Mechanisms for detection, reporting, and correction of any sampling or analytical problems should be developed and maintained. These QC procedures should be audited through data review and blind quality assurance analyses.

In a general monitoring program, QA activities will focus on: 1) sampling, 2) analysis, 3) method verification, and 4) sample management. Examples of the quality assurance and quality control aspects to be considered for a monitoring program are discussed for these four areas. Guidelines for specific quality assurance protocols can be found in the EPA quality control/quality assurance and laboratory practice guideline documents listed in the references (3-3 to 3-18).

3.2 SAMPLING QUALITY CONTROL

Detailed quality assurance procedures are essential to the successful completion of sampling activities. The objectives of a sampling quality assurance program are to:

- evaluate all aspects of the sampling methodology, and
- identify problems as they occur.

The items to be addressed when developing specific QC procedures for sampling include:

- facilities and equipment inventory,
- training program,
- document control,
- quality control charts,
- supervision,
- materials inventory and procurement,
- reliability and maintenance,
- data validation,
- equipment calibration, and
- correlation tests.

The types of sampling QC procedures which would be implemented include:

- Instructions which insure proper implementation of the monitoring program design, correct use of all equipment, and adherence to sampling protocols.
- Standardized data forms developed for each specific sampling activity to aid in sampling documentation and record keeping. The use of formatted data forms helps minimize recording errors and insures complete data.
- Quality control tests, i.e.:
  - calibration checks at regular intervals,
  - use of blank or control samples to check for interferences and contamination,
  - field spiking to evaluate recoveries,
  - replicate and multiple time samples to evaluate the sources of variation, and
  - sampling checks for standardization of equipment and personnel.
- Statistical analysis should be conducted and quality control results reported during sampling activities. The quality control tests should be followed by prompt determination of results. If contamination of samples is occurring, it is desirable to learn this before many samples have been taken. Specific reporting of quality control data aids in continual documentation of performance and allows rapid feedback of QC results to sampling personnel for corrective action.

- Independent quality assurance audits of field sampling tasks to insure adherence to sampling protocols, experimental design, and quality control procedures. Audit procedures include checklists of key procedure items, review of completed data forms, and initiation of additional quality control samples such as standards and controls.
- Where possible, alternative sampling and analysis methods provide added definition and control of data accuracy. Statistical correlation techniques can be used to determine if results from the two methods are identical within expected experimental reproducibility.

These procedures may be modified for each type of sample or analysis in the monitoring plan. For example, duplicate samples may be grab samples collected at the same time, dual test runs, splits of composite samples, or samples from similar process locations. Blanks must be analyzed to determine analytical background arising from reagents, distilled water handled in the field, and resins for collection of organics from gases.

3.3 ANALYTICAL QUALITY CONTROL

The quality control procedures for all analytical methods in the monitoring program are critical for obtaining reliable and consistent data. Analytical QC practices include the use of standard methods when available, calibrations, analysis of standard reference materials, and the frequent analysis of QC check samples.

The quality control of all test results can be directly related to proper calibration procedures. Calibration procedures and standards should be specified for all equipment and supplies used. Traceability to common standards is essential if analytical procedures are conducted in multiple laboratories. Quality assurance procedures for standards and calibration include the following:

- written, detailed calibration instructions,
- preparation procedures for secondary standards, when applicable,

- requirements for frequency of calibration,
- record keeping of all calibrations and standards used,
- quality control charts for recording results from multiple calibrations,
- evaluation of internal standards,
- tolerances for calibration requirements,
- action when calibration requirements are not met.

All calibration results should be included in the data base for review and statistical analyses.

Each analytical protocol should have detailed requirements for equipment and supplies. Reagents, solvents, and standards with specific levels of purity should be defined within the monitoring program. Resins, GC column materials, glassware, and sample handling equipment should also be specified. The quality control procedures for equipment and supplies include the following:

- checklists for required supplies,
- documentation and reporting of all deviations from specified equipment,
- procedures for testing for purity of reagents,
- tolerances for glassware, when applicable,
- purchasing high-purity distilled-in-glass solvents in large quantities from a single lot,
- cleaning of glassware with chromic acid or firing in a kiln, and
- use of organic free water when appropriate.

Routine quality control samples analyzed concurrently with samples will be a significant portion of laboratory quality control efforts. The purpose of these checks are twofold:

- to assure that samples being analyzed satisfy predetermined standards of accuracy, and

- to measure and document actual levels of accuracy and precision.

There are many different types of quality assurance samples which could be used for these purposes. The correct combination will depend on the economics and complexity of the analytical method and the desired degree of accuracy. The following quality control parameters are general considerations for field and laboratory analyses:

- Interferences - The analytical results may be affected by interferences from the glassware, solvents, reagents, sample handling or sample matrix. Blank samples subjected to conditions similar to actual samples can be used to evaluate interferences from procedures, equipment or reagents. Frequency of blank analysis will depend on the extent of the interference indicated by initial results and on the frequency of restocking reagents and supplies. Blanks should be run routinely for impinger solutions, organic collection resins, filters and extraction solvents. Positive or negative interferences may also arise from components in the sample matrix. Methods should be verified for each matrix as discussed in Section 3.4 and periodically checked, particularly if changes in the process operations indicate potentially significant changes in the sample matrix.

- Recovery - The accuracy of much analytical data is directly related to the efficiency of analyte recovery through the various steps in a measurement or preparative procedure such as extraction or purging. Recovery can be measured using internal standards or spiked samples which are analyzed as any other sample. Recovery efficiencies should be determined to define deviations and compared to accuracy requirements for each measurement technique.

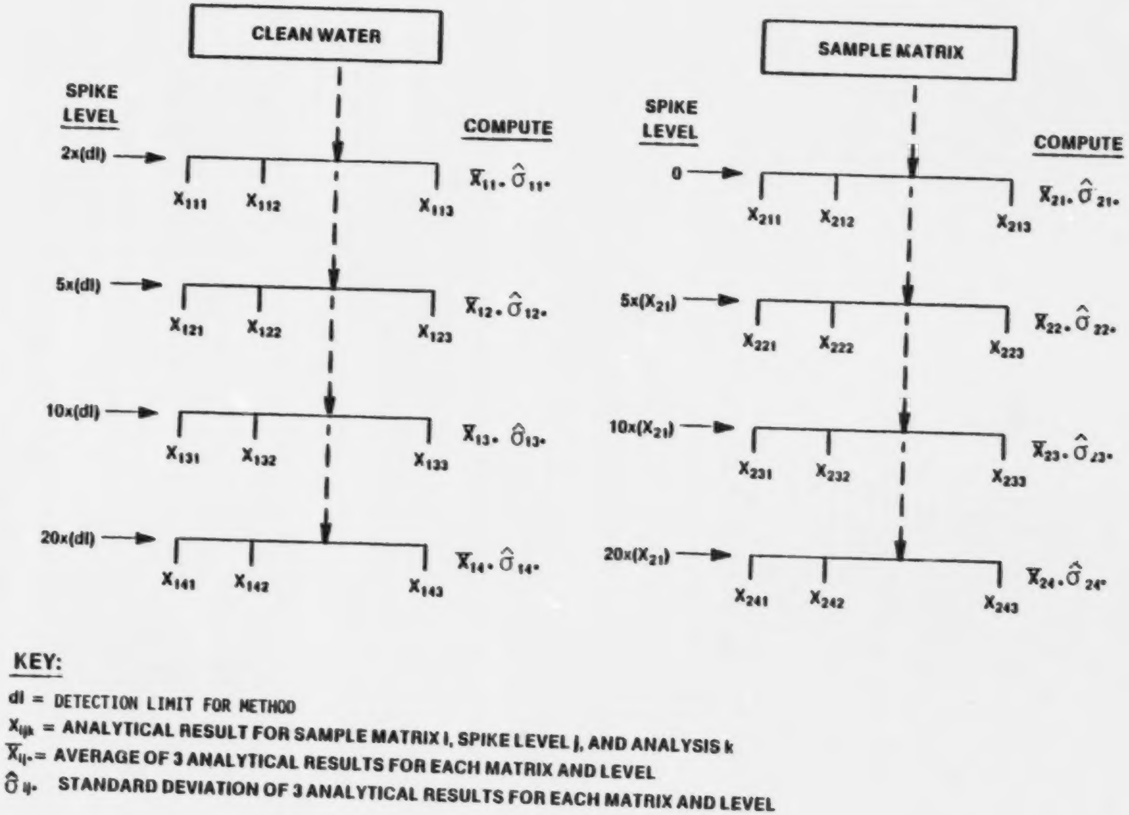
- Precision - The precision or repeatability of a method is required for proper interpretation and weighting of the resulting data. Repeat samples or standards can be used to determine precision on a regular basis. The difference between replicate analyses should be compared against predetermined precision limits for acceptability. If repeated analyses are not possible, for example with on-line process GC analyses, then moving-ranges can be used to measure precision. The precision may be reported as a standard deviation of repeatability statistic and may depend on the concentration of the analytes.

- Reproducibility - The reproducibility of a method refers to the repeatability over a period of time. How well will analyses repeated a month later agree with today's results? Reproducibility will be measured by repeated analysis of samples from a previous time period.
- Qualitative Specificity - In complex sample matrices with multiple compounds, the use of some methods, such as GC, can lead to misidentification of compounds. The extent of misidentification can be estimated by repeated analysis of standards containing compounds of interest. Confirmation by alternate methods, such as GC-MS provide a basis to evaluate misidentification problems.

The QA plan should include procedures for establishing a "closed loop" mechanism for analyzing QC data, reporting, and correcting problem areas. QC reports should be sent regularly to appropriate personnel. Forms and procedures will document QC results, report the results to the QA Coordinator or monitoring project management, and document corrective actions taken to expedite the production of meaningful data.

3.4 METHOD VERIFICATION

Analytical methods for a specific monitoring program should be verified for application to expected sample matrices through a formal verification procedure. Figure 3-1 summarizes an example verification procedure. This verification will give accuracy and precision estimates for each method and determine if the accuracy and precision are dependent on the concentration levels and/or sample matrix effects. Each verification requires 24 analyses by the method. Modifications to this example protocol may be required for some specific methods. In the general verification protocol for aqueous samples, clean water is spiked at levels of 2, 5, 10 and 20 times the detection limit of the method. Each spiked sample is analyzed three times. A


CLEAN WATER
SPIKE LEVEL
COMPUTE
2x(dl)
X_{111} X_{112} X_{113}
$\overline{X}_{11\cdot}, \hat{\sigma}_{11\cdot}$
5x(dl)
X_{121} X_{122} X_{123}
$\overline{X}_{12\cdot}, \hat{\sigma}_{12\cdot}$
10x(dl)
X_{131} X_{132} X_{133}
$\overline{X}_{13\cdot}, \hat{\sigma}_{13\cdot}$
20x(dl)
X_{141} X_{142} X_{143}
$\overline{X}_{14\cdot}, \hat{\sigma}_{14\cdot}$
SAMPLE MATRIX
SPIKE LEVEL
COMPUTE
0
X_{211} X_{212} X_{213}
$\overline{X}_{21\cdot}, \hat{\sigma}_{21\cdot}$
5x(X_{21})
X_{221} X_{222} X_{223}
$\overline{X}_{22\cdot}, \hat{\sigma}_{22\cdot}$
10x(X_{21})
X_{231} X_{232} X_{233}
$\overline{X}_{23\cdot}, \hat{\sigma}_{23\cdot}$
20x(X_{21})
X_{241} X_{242} X_{243}
$\overline{X}_{24\cdot}, \hat{\sigma}_{24\cdot}$

KEY:

dl = DETECTION LIMIT FOR METHOD

X_{ijk} = ANALYTICAL RESULT FOR SAMPLE MATRIX i, SPIKE LEVEL j, AND ANALYSIS k

$\overline{X}_{ij\cdot}$ = AVERAGE OF 3 ANALYTICAL RESULTS FOR EACH MATRIX AND LEVEL

$\hat{\sigma}_{ij\cdot}$ STANDARD DEVIATION OF 3 ANALYTICAL RESULTS FOR EACH MATRIX AND LEVEL

Figure 3-1. Example method verification scheme

process sample for which the method is intended should be obtained and analyzed in triplicate. The average of these analyses (x_{21}) will be used to determine spiking levels for the parameter of interest. This general verification approach is applicable to vapor phase impinger collection techniques (the impinger solution is spiked). For resin collection techniques an analogous verification approach can be implemented

The data from verification studies can be analyzed statistically to determine:

- the type of error (constant versus proportional to concentration)
- accuracy (measured concentration versus spikes)
- precision (variation in measured concentrations)
- matrix effects (compare precision and accuracy of sample to spiked clean water).

The results should be summarized as part of a written procedure for the specific method.

3.5 SAMPLE MANAGEMENT

The control of storage and handling of samples is an important part of the QA system. Samples should be tracked from the time they are collected through storage and analysis.

The sample management and tracking identifies information in three areas for each sample collected:

- time of collection and basic description,
- sample status (location, splits),

- analytical status of sample (analyses to be done and analyses completed).

A master log of all process samples should be maintained for sample coordination and data evaluation.

3.6 REFERENCES FOR SECTION 3

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SECTION 4

SOURCE MONITORING

This section presents an approach to the development of the source monitoring portion of an effective, site-specific monitoring plan for a synthetic fuels facility receiving assistance from the Synthetic Fuels Corporation. The types of sources covered by this monitoring plan include: 1) controlled discharges of process effluents from discharge structures such as stacks, pipes, or flares and 2) fugitive releases from processing, transportation, storage or impoundment facilities for feedstocks, products or solid/liquid wastes.

As indicated in the Congressional explanation of the Energy Security Act, Section 131(e) (reproduced in part in Section 1.0), it is intended that environmental and health-related monitoring conducted pursuant to this section should "characterize and identify areas of concern and develop an information base for the mitigation of problems associated with replication of synthetic fuels projects." Thus, the objective of the monitoring program to be conducted at each synthetic fuels facility receiving assistance is to develop a data base. This data base must be adequate to characterize significant sources of discharges to the environment. It also must provide a basis to help mitigate problems in future facilities. To provide a comprehensive identification of "areas of concern", the data on emissions and discharges must be representative of major operating situations encountered during the life of the plant and must address both regulated and unregulated substances.

Mitigation of "problems associated with the replication of synthetic fuels projects" can be accomplished through both administrative and technical solutions. To support administrative solutions by state and federal regulatory or permitting agencies, the data base should be adequate to identify situations which can be resolved in future projects by different permit conditions, changes in existing regulations or development of new regulations. To support technical solutions, the data base must be adequate to characterize the capabilities of existing pollution control technologies and to identify needs for developing modified or new control technologies.

Construction and operating permits issued by the various local, state and federal agencies will require monitoring of emissions and discharges to the environment. Such monitoring will be done to demonstrate compliance with limitations and performance requirements set forth in the permits. These requirements will depend on both the location and design of the facility. This section outlines the general source monitoring requirements needed to develop a data base responding to the objectives discussed above for both regulated and unregulated pollutants. As a practical matter, most of the compliance monitoring required by permits for new facilities will be included in this manual. However, the monitoring approach described here does not necessarily include all permit monitoring requirements, nor is the approach suggested here guaranteed to be consistent with every conceivable set of permit requirements. Permit monitoring requirements will be set by the cognizant agency based on site-specific conditions. Accordingly, any suggestions in this manual in conflict with permit monitoring requirements are superceded by the permit requirements. Permit-required or compliance monitoring is expected to be a major source of the long term discharge characterization data needed to fulfill a significant portion of the data base requirements.

Development of the source monitoring portion of a plan for monitoring "environmental and health-related emissions" requires that a number of decisions be made:

- selecting the streams and species to be monitored;
- determining process and control technology performance data to support the discharge stream data;
- selecting the timing, frequency and duration of measurements;

- selecting techniques and procedures for making the necessary measurements; and

- selecting procedures for validating and analyzing the acquired monitoring data.

The following sections provide suggestions, approaches and procedures to aid in these decisions. These are general discussions that apply to a number of synthetic fuels technologies including: oil shale mining and retorting, direct and indirect coal liquefaction, coal gasification, and tar sands (heavy oil) recovery. Although this manual does not address all synthetic fuels processes explicitly (for example monitoring needs associated with peat processing are not discussed in detail) it is structured to be applicable to any fossil fuel conversion process. The development of an environmental monitoring plan is a very complex and highly site-specific task. The recommendations and approaches given in this non-site-specific document will have to be tailored by a facility operator to develop a plant-specific monitoring plan.

To simplify the discussion of discharge streams for this wide variety of technologies, generic stream categories have been developed. These are described in Section 4.1 along with monitoring suggestions for each category. A generic category includes the streams from each technology which have similar characteristics, compositions and monitoring requirements. The monitoring suggestions for a complete data base are then presented in the form of substance or property measurement needs for each generic stream category. In most cases, the suggestions are to measure specific chemical substances or properties. However, due to the large number of organic compounds of potential concern, survey analytical techniques that measure more than one component of a class are suggested for many organics. If properly executed, these techniques will provide data on the majority of compounds of environmental or health concern.

A general discussion of control technology performance monitoring is also presented in Section 4.1. This discussion includes the characteristics of many of the control technologies which will be used in synthetic fuels facilities. Recommended approaches for developing monitoring plans to characterize removal efficiency for the design pollutant as well as other pollutants of concern are provided. The design of a particular facility, performance data availability and proprietary data restrictions will have a major influence on the control technology monitoring aspects of any specific plan.

Alternative approaches for implementing the monitoring suggestions for the data base described in Section 4.1 are given in Sections 4.2 and 4.3. In general, the alternatives describe options for phasing the monitoring effort. A phased monitoring effort will allow the data base to be developed in the most cost-effective manner. Other alternatives or phasing options which might be suggested by those preparing specific monitoring plans should be acceptable as long as they provide a data base covering major operating situations in the detail needed to respond to the intent of Section 131(e).

A two phase approach for developing the data base is described in some detail in Section 4.2. Phase 1 of this suggested approach involves an intensive monitoring effort to develop a complete data base representing "normal" plant operating conditions. Phase 1 would be conducted for some initial period after plant shakedown. Preparation for Phase 1 monitoring is accomplished during the start-up and shakedown period. Phase 2 involves a lower level-of-effort, long-term monitoring program in which a limited number of "indicator" species/parameters are monitored to "track" the data base defined in Phase 1. During Phase 2, the detailed Phase 1 characterization would be repeated when significant deviations from the conditions characterized in Phase 1 are observed through changes in indicators.

Section 4.2 also shows how statistical principles can be used to define the frequency and duration of monitoring. For the phased monitoring approaches, Section 4.2 suggests that statistical techniques can be used to analyze Phase 1 data and develop a Phase 2 monitoring plan design (i.e., to select indicator species for Phase 2 monitoring). However, the extent and nature of the data base collected in Phase 1 cannot be defined beforehand. It is possible that the results of Phase 1 data collection could fail to provide a statistical basis for the selection of indicator species for many important variables. If so, then an alternate approach to selecting Phase 2 monitoring parameters might be required. Some of these alternate approaches are discussed in Sections 4.2 and 4.3.

In Section 4.4, alternative measurement techniques and procedures are presented for each of the species or properties suggested for inclusion in the data base. Information is provided in enough detail to allow the initial selection of monitoring procedures for a monitoring plan. However, conditions encountered in a particular facility and the potential for interferences require that the techniques be verified in preparation for Phase 1 monitoring. It is likely that stream conditions or data quality control objectives will require that at least some of the procedures be modified.

4.1 DISCHARGE STREAM AND CONTROL TECHNOLOGY DATA BASE SUGGESTIONS

The monitoring suggestions outlined in this section are designed to provide the total data base needed to characterize discharges and control technologies and to derive administrative and technical solutions to "replication" problems. This includes both data required to comply with the provisions of environmental permits and data on nonregulated pollutants.

This section presents information to aid in developing detailed source specific monitoring plans. It identifies the discharge streams of interest (Section 4.1.1) and what data are desired for, or what species should be measured in, each stream (the "total" data base, Section 4.1.2). Section 4.1.3 discusses control technology monitoring.

4.1.1 Discharge Streams of Interest

The synfuel technologies addressed in this manual include coal gasification, direct and indirect coal liquefaction, oil shale mining and retorting, and heavy oil production from tar sands. Based on a review of proposed designs and publicly available data, a large number of potential discharge streams were identified. But even though the discharge streams arise from different technologies or different parts of a facility, they have some characteristics in common. Because of these similarities and the desire to simplify the presentation of data needs in this manual, generic categories of discharge streams were defined. A generic category is a group of streams with similar characteristics and hence similar data needs.

The fifteen generic categories of discharge streams are presented in Tables 4-1 through 4-3 for gases, liquids, and solids, respectively. The tables show: 1) examples of the types of streams in each generic category, 2) components of interest (environmentally significant species) in those streams, 3) the synfuels technologies that would be expected to generate the discharge streams, and 4) clarifying comments. In some designs the example streams may be routed to control devices. In these cases, the treated discharge should be considered for monitoring.

The information telling which synfuels technologies would generate the example waste streams is based on an estimate of the probability ("usually", "sometimes", or "rarely") that a stream will be found in a plant employing the indicated technology. Of course, the presence or absence of a stream in a specific facility will depend on the design. For example, all synfuels technologies generate process-derived wastewater, but the design of the plant water management system determines whether the wastewater is treated and discharged to an outfall or reused within the plant.

TABLE 4-1. GENERIC CATEGORIES - GASEOUS DISCHARGE STREAMS

Generic Stream Categories and Examples of Streams Found in each Category	Environmentally Significant Species Potentially Present	Synfuels Technologies in which Discharge Stream May be Found (see note a)				Comments
		Coal Gasification or Indirect Liquefaction	Direct Liquefaction	Oil Shale	Tar Sands	
1. Boiler/furnace flue gases resulting from the combustion of conventional fuels such as coal, fuel oil and natural gas.	Criteria pollutants^b; Possible trace elements (depends on fuel)	1	1	3	3	This stream category will be a major potential source of criteria pollutant emissions and may be regulated as such. Emissions from these types of sources have been well characterized previously.
2. Boiler/furnace/incinerator flue gases resulting from the combustion of process-derived fuels or waste streams such as:	Criteria pollutants^b; Possible trace elements (depends on fuel) Possible trace organics, reduced sulfur species and reduced nitrogen species (depends on fuel and combustor performance)					Fuels in this generic category originate in a process unique to a synthetic fuels facility. Emissions from these sources generally are not well characterized. Mixed fuel combustors burning both conventional and process-derived fuels should be treated as category 2 combustors for purposes of monitoring. Some flue gases will contain organics and others will not, depending on combustion/incineration efficiency.
a. flue gases from fuel-gas-fired furnaces		1	3	3	3	
b. flue gases from synthetic distillate-fired furnaces		2	1	3	3	
c. flue gases from furnaces burning by-product tars and oils		2	2	1	1	
d. flue gases from waste gas incinerators		2	2	2	2	
e. flue gases from sludge incinerators		2	2	2	2	
f. flue gases from wastewater incinerators		2	2	2	2	

(Continued)

TABLE 4-1. (continued)

Generic Stream Categories and Examples of Streams Found in each Category	Environmentally Significant Species Potentially Present	Synfuels Technologies in which Discharge Stream May be Found (see note a)				Comments
		Coal Gasification or Indirect Liquefaction	Direct Liquefaction	Oil Shale	Tar Sands	
3. Uncombusted vent gases (monitored directly if vented, monitored before combustion if flared)	Reduced sulfur and nitrogen species, CO, organics, possible trace elements, possible particulates					Unlike the previous two categories, these streams may contain significant quantities of organics and reduced sulfur and nitrogen species.
a. coal feeder vent gas		2	2	3	3	
b. transient routine vent gases		1	2	1	2	
c. startup/upset vent gases		1	2	1	2	
d. sulfur recovery system tail gases		1	1	1	1	
e. CO_2-rich vent gas from selective AGR		1	1	2	2	
4. Tank vents	Dissolved gases, VOC, reduced sulfur and nitrogen species					These streams will contain volatile species present in the stored fluids.
a. product storage		2	1	1	1	
b. by-product storage		2	2	2	2	
c. process storage/ surge tanks		1	1	1	1	
5. Process fugitive emissions	CO, VOC, reduced sulfur and nitrogen species					These types of emissions have been well characterized in the petroleum refining and petrochemical industries; however the frequency and composition might vary for synfuels facilities. Very little data are available on nonhydrocarbon emissions.
a. pump and compressor seal leaks		1	1	1	1	
b. valve and flange leaks		1	1	1	1	

(Continued)

TABLE 4-1. (continued)

Generic Stream Categories and Examples of Streams Found in each Category	Environmentally Significant Species Potentially Present	Synfuels Technologies in which Discharge Stream May be Found (see note a)				Comments
		Coal Gasification or Indirect Liquefaction	Direct Liquefaction	Oil Shale	Tar Sands	
6. Fugitive gaseous and particulate emissions from waste impoundment, storage or disposal facilities	Particulates (depends on source) dissolved gases, VOC, reduced sulfur and nitrogen species					These waste streams are distinguished from those in category 7 (below) by the fact that they contain volatile or reactive species.
a. wastewater storage ponds and treatment vessels		1	1	1	1	
b. storage, treatment and disposal facilities for solid waste containing volatile organics, e.g., sludge landfarms		1	1	1	1	
7. Fugitive particulate emissions	Particulates					Some of these sources will not be present in facilities employing in-situ processing.
a. oil shale mining/hauling		3	3	1	3	
b. feed storage		1	1	1	1	
c. crushing, screening, sizing and conveying operations		1	1	1	1	
d. solids (e.g., dry ash, slag) impoundment and disposal areas		1	1	1	1	

[a] Codes refer to probability of occurrence: 1 = usually found; 2 = may be found depending upon the conversion processes or design approaches used in a specific facility; 3 = seldom found.

[b] Criteria Pollutants include SO_2, NO_x, CO, particulate matter, ozone and lead.

TABLE 4-2. GENERIC CATEGORIES - AQUEOUS DISCHARGE STREAMS

Generic Stream Categories and Examples of Streams Found in Each Category	Environmentally Significant Species Potentially Present	Synfuels Technologies in which Discharge Stream May be Found (see note a)				Comments
		Coal Gasification or Indirect Liquefaction	Direct Liquefaction	Oil Shale	Tar Sands	
1. Wastewaters discharged to outfalls, impoundments, or deep wells that are not unique to synfuels plants and have their origins in an organic-laden environment. Source of the raw wastewaters which comprise this category include:	Water quality parameters^b, extractable aliphatics and aromatics, trace elements					This category includes organics-containing waste streams with characteristics similar to those of analogous waste streams from non-synfuels facilities.
a. sanitary sewer wastes		1	1	1	1	
b. some laboratory wastes		1	1	1	1	
c. some equipment cleaning wastes		1	1	1	1	
2. Wastewaters discharged to outfalls, impoundments, or deep wells that are not unique to synfuels plants and have their origins in an organic-lean environment. Sources of the raw wastewaters which comprise this category include:	Water quality parameters^b, trace elements					This category includes organic-lean waste streams with characteristics similar to those of analogous waste streams from non-synfuels facilities.
a. demineralizer regeneration wastes		1	1	1	1	
b. cooling tower blowdown (if fresh water is only source of makeup)		1	1	1	1	
c. coal pile runoff		1	1	3	3	
d. boiler blowdown		1	1	1	1	
e. boiler ash/slag quench or sluice water blowdown		2	2	3	3	
f. runoff from dust control		2	2	2	2	

(Continued)

TABLE 4-2. (continued)

Generic Stream Categories and Examples of Streams Found in Each Category	Environmentally Significant Species Potentially Present	Synfuels Technologies in which Discharge Stream May be Found (see note a)				Comments
		Coal Gasification or Indirect Liquefaction	Direct Liquefaction	Oil Shale	Tar Sands	
3. Wastewaters codisposed with solid wastes or discharged to outfalls, impoundments or deep wells that result from the quenching, cooling, upgrading, etc. of the plant's main product streams. Sources of the raw wastewaters which comprise this category include:	Water quality parameters,[b] dissolved gases, trace elements, trace organics.					This category includes a number of high volume waste streams which (in raw form) will tend to be unique to the synfuels technology from which they originate. Generally, these streams have not been well characterized to date, so this category is of major interest in source monitoring. These streams are different from those included in category 4 (below) because they are likely to contain organic as well as inorganic contaminants at levels of interest. The nature of the discharge stream resulting from the treatment of these wastes will be highly variable depending upon the nature of the raw waste, the array of treatment technologies used and the extent of water recycle/reuse in the facility.
a. raw product separation condensates/quench waters (e.g. Lurgi gas liquor, EDS cold separator water, retort water)		1	1	1	1	
b. product purification/upgrading condensates (e.g. sour water from atmospheric or vacuum fractionation, sour water from oil, naphtha or solvent hydrogenation, AGR condensates and blowdown solvents).		1	1	1	1	
c. product upgrading wastewaters (e.g. methanol or F-T synthesis condensates).		2	2	2	2	
d. process area runoffs		1	1	1	1	

(continued)

TABLE 4-2. (continued)

Generic Stream Categories and Examples of Streams Found in Each Category	Environmentally Significant Species Potentially Present	Synfuels Technologies in which Discharge Stream May be Found (see note a)				Comments
		Coal Gasification or Indirect Liquefaction	Direct Liquefaction	Oil Shale	Tar Sands	
4. Wastewaters codisposed with solid waste or discharged to outfalls, impoundments or deep wells that are unique to synfuels facilities but are not included in category 3 above. Sources of the raw wastewaters which comprise this category include:	Water quality parameters,[b] trace elements, dissolved gases					These wastewaters are distinguished from those included in category 3 by their origin in a portion of the process which does not come into contact with any raw or upgraded product streams containing high concentrations of water soluble organics.
a. methanation condensates		2	2	3	3	
b. gasifer ash/slag quench or sluice system blowdown		1	2	3	3	
c. sulfur recovery system tail gas treatment condensates		2	2	2	2	
d. runoff from oil shale mining/storage operations (overburden piles)		3	3	2	3	
e. collected leachate from solid waste landfill sites		2	2	2	2	

[a] Codes refer to probability of occurrence: 1 = usually found; 2 = may be found depending upon the conversion processes and design approaches used in a specific facility, 3 = seldom found.

[b] Water quality parameters of interest in synfuels facilities are listed in Table 4-7.

TABLE 4-3. GENERIC CATEGORIES - SOLID DISCHARGES

Generic Stream Categories and Examples of Streams Found in Each Category	Environmentally Significant Species Potentially Present	Synfuels Technologies in which Discharge Stream May be Found (see note a)				Comments
		Coal Gasification or Indirect Liquefaction	Direct Liquefaction	Oil Shale	Tar Sands	
1. Organic-laden solid wastes not unique to synfuels facilities.	Leachable organics and inorganics, ignitability (coal fines), trace elements					Categories 1 and 2 both contain streams that are expected to be similar to analogous waste streams in related industries for which some characterization information has been gathered. The main difference between these categories is that the category 1 streams are expected to contain low levels of organics.
a. biological oxidation sludge from treatment of sanitary sewage		2	2	2	2	
b. collected dust (feed solids)		1	1	1	3	
c. excess coal fines		2	2	3	3	
2. Organic-free or organic-lean solid wastes not unique to synfuels plants.	Trace elements					
a. ashes from combustors burning conventional fuels		1	1	3	3	
b. FGD sludges		2	2	2	2	
c. makeup water treatment sludges.		1	1	1	1	
d. oil shale mining overburden		3	3	2	3	

(Continued)

TABLE 4-3. (continued)

Generic Stream Categories and Examples of Streams Found in Each Category	Environmentally Significant Species Potentially Present	Synfuels Technologies in which Discharge Stream May be Found (see note a)				Comments
		Coal Gasification or Indirect Liquefaction	Direct Liquefaction	Oil Shale	Tar Sands	
3. Organic-laden solid wastes unique to synfuels facilities.	Leachable and extractable organics and inorganics, ignitability, reactivity, trace elements					Category 3 and 4 waste streams are distinguished from those in categories 1 and 2 (above) by their origin. They originate in a unit operation which is either unique to a synfuels plant or has some features which are unique. Very limited characterization data on most of these types of streams have been gathered to date. Most of the waste streams in category 3 result from the treatment of process derived wastewaters containing high concentrations of organics (category 3 streams in Table 4-2). Category 4 streams should contain very low levels of organics because they were subjected to a high temperature, oxidizing regime before release.
a. biological treatment sludge from treatment of process wastewaters		2	2	2	2	
b. oil/process water separation sludges and spent filter media		1	1	1	1	
c. excess raw shale fines		3	3	1	3	
d. processed shale/sands/char (carbonaceous retorted shale)		2	2	1	1	
4. Organic-free or organic-lean solid wastes unique to synfuels plants.	Trace elements, extractable aliphatics and aromatics					
a. gasifer ash/slag		1	2	3	3	
b. incinerator solids/brines		2	2	2	2	
c. spent catalysts		2	2	2	2	
d. decarbonized retorted shale		3	3	1	3	
e. byproduct sulfur if treated as solid waste		2	2	2	2	

[a] Codes refer to probability of occurrence: 1 = usually found; 2 = may be found depending upon the conversion processes and design approaches used in a specific facility, 3 = seldom found.

Several criteria were used to develop the generic categories. First, the streams were grouped according to physical state, i.e., gaseous, aqueous, or solid. Then the streams were subgrouped according to composition. Often, the main distinguishing factor was the presence or lack of organics. Finally, streams were grouped on the basis of uniqueness to synfuels technologies. For example, treated wastewaters originally derived from raw reactor effluent cooling are considered unique to synfuels facilities, while flue gases from onsite coal combustion are not. (Coal combustion gases should be similar to the flue gases from any coal-fired boiler firing the same coal.)

The reason for separating unique and nonunique streams is that greater emphasis is placed on monitoring suggestions for unique streams. It is the unique streams for which the least amount of information is publicly available. This approach is not intended to imply that the nonunique streams are unimportant or that monitoring of these streams is not desirable. It simply reflects the facts that (1) more is known about the nonunique streams, (2) monitoring of nonunique streams may be clearly required by law or permit, and (3) facility designers and permit reviewers are more experienced in developing monitoring plans for these streams.

Although there are many differences in the processing sequences and equipment used in synfuels facilities, the five technologies considered here can be represented generally by the block flow diagram in Figure 4-1. While this diagram does not cover technology variations in detail, it shows in general the major sources of waste streams expected from these facilities (as listed in Tables 4-1 through 4-3).

As shown in Figure 4-1, raw feed (coal, shale or tar sands) received from the mine may undergo pretreatment steps such as crushing and sizing (feed preparation) to generate a feedstock suitable for the main reactors. In the main reactors, the prepared feed reacts with other feed materials such as steam, oxygen, hydrogen, hot water, hot combustion gases or pyrolysis product gases. These reactions generally produce a raw reactor effluent stream (raw product or synthesis gas), and a mineral residue (e.g., ash, char, spent shale

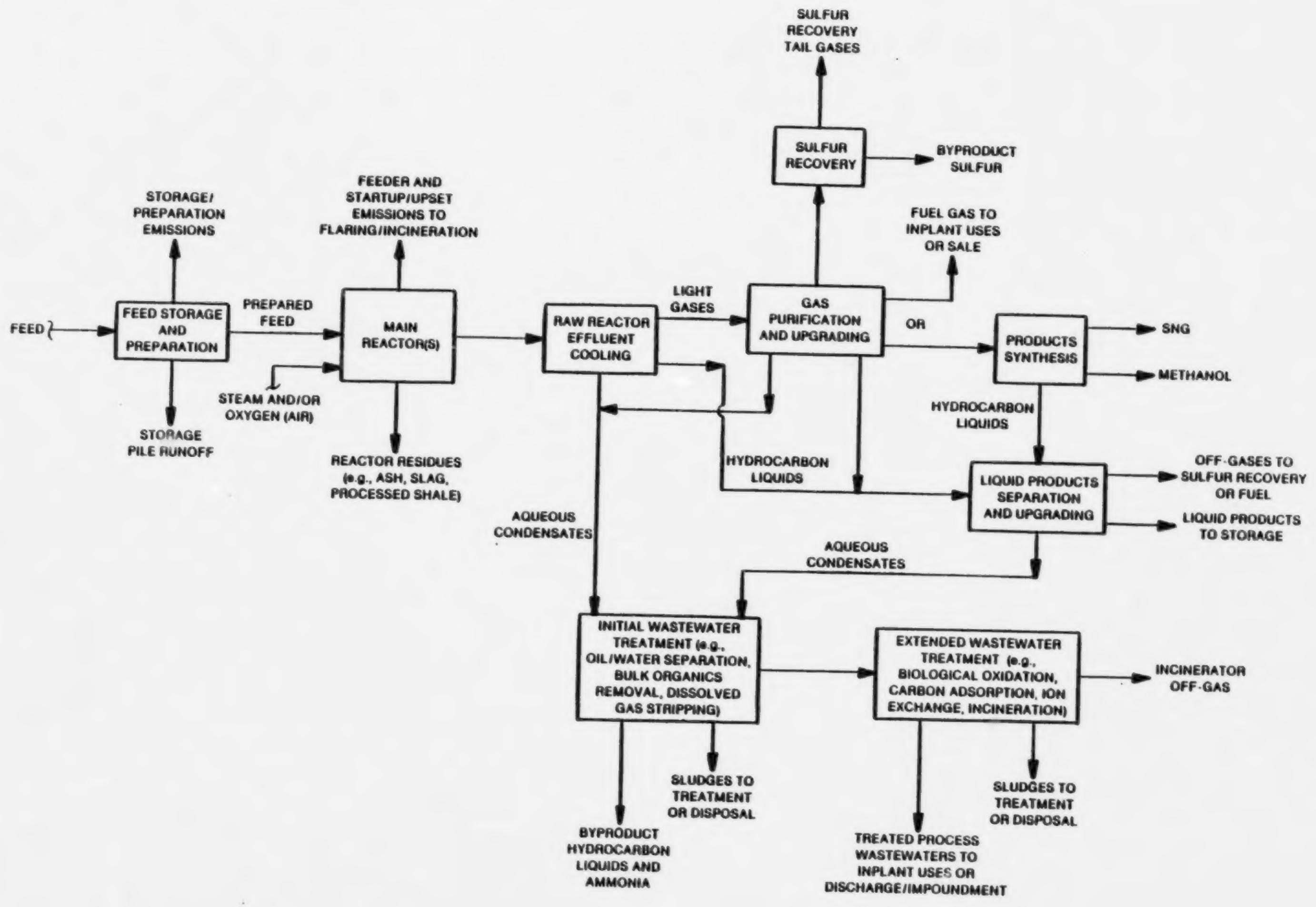
SULFUR RECOVERY TAIL GASES
SULFUR RECOVERY
BYPRODUCT SULFUR
STORAGE/ PREPARATION EMISSIONS
FEEDER AND STARTUP/UPSET EMISSIONS TO FLARING/INCINERATION
FUEL GAS TO INPLANT USES OR SALE
FEED
FEED STORAGE AND PREPARATION
PREPARED FEED
MAIN REACTOR(S)
RAW REACTOR EFFLUENT COOLING
LIGHT GASES
GAS PURIFICATION AND UPGRADING
OR
PRODUCTS SYNTHESIS
SNG
METHANOL
STEAM AND/OR OXYGEN (AIR)
STORAGE PILE RUNOFF
REACTOR RESIDUES (e.g., ASH, SLAG, PROCESSED SHALE)
HYDROCARBON LIQUIDS
HYDROCARBON LIQUIDS
LIQUID PRODUCTS SEPARATION AND UPGRADING
OFF-GASES TO SULFUR RECOVERY OR FUEL
LIQUID PRODUCTS TO STORAGE
AQUEOUS CONDENSATES
AQUEOUS CONDENSATES
INITIAL WASTEWATER TREATMENT (e.g., OIL/WATER SEPARATION, BULK ORGANICS REMOVAL, DISSOLVED GAS STRIPPING)
EXTENDED WASTEWATER TREATMENT (e.g., BIOLOGICAL OXIDATION, CARBON ADSORPTION, ION EXCHANGE, INCINERATION)
INCINERATOR OFF-GAS
SLUDGES TO TREATMENT OR DISPOSAL
SLUDGES TO TREATMENT OR DISPOSAL
BYPRODUCT HYDROCARBON LIQUIDS AND AMMONIA
TREATED PROCESS WASTEWATERS TO INPLANT USES OR DISCHARGE/IMPOUNDMENT

Figure 4-1. Generalized block flow diagram of synthetic fuels facilities.

or spent sands). An alternative processing scheme, in situ processing, avoids several of these unit operations by using the original resource formation as the reaction vessel. With this approach, the main reactant is injected into the formation (after fracturing in the case of coal or oil shale) and the produced raw products are withdrawn from the formation through another well.

Hot, raw products from the main reactors generally undergo a series of quenching and cooling steps which produce a condensed wastewater and gaseous and/or hydrocarbon-rich liquids stream(s). The gaseous and hydrocarbon liquids streams undergo further processing including purification (e.g., removal of acid gases such as H_2S and CO_2 from the gaseous stream), separation (e.g., flashing and distillation cf hydrocarbon liquids), and some upgrading (e.g., gas oil hydrogenation). In indirect coal liquefaction, the purified and upgraded gaseous stream is further processed to produce liquid hydrocarbons (e.g., Fischer-Tropsch synthesis).

In addition to the main processing sequence, Figure 4-1 also shows two important pollution control systems - sulfur recovery and wastewater treatment. The sulfur recovery system processes sulfur containing gases (H_2S-containing gases removed from fuel-rich gas streams by acid gas removal units and dissolved H_2S stripped from wastewater) and produces by-product sulfur and a desulfurized tail gas for discharge to the atmosphere. The wastewater treatment system receives wastewaters from various parts of the plant (e.g., raw product cooling and liquids product separation and upgrading). The wastewaters are treated, as appropriate, for removal of: 1) suspended solids, tars, and oils, 2) bulk organics, 3) dissolved gases, 4) residual organics, and 5) dissolved solids. The processes and sequencing in the wastewater treatment system are determined mainly by two factors - the composition of the untreated wastewaters and the desired quality of the treated waters (which is dependent on whether they will be reused, discharged, or impounded).

Auxiliary systems needed to support the main process operations are not shown in Figure 4-1. Auxiliaries which could be present include steam and electricity generation, cooling water system(s), air separation units, raw water treatment, product/by-product storage facilities, and waste treatment operations such as flares, incinerators and solid waste disposal facilities. Also omitted from Figure 4-1 is the mining operation often present in conjunction with these facilities, especially for oil shale and tar sands operations.

4.1.2 Discharge Stream Data Base Suggestions

Tables 4-4, 4-5, and 4-6 show suggested monitoring that would define the total data base for the species and properties of interest in each generic category of gaseous, aqueous and solid discharges. The monitoring suggested in these tables represents the total data base. Comments are given to explain why each type of monitoring is suggested, to qualify the general requirements, or to identify data needs of particular interest. Table 4-7 provides a specific listing of water quality parameters which are referenced as a group in Table 4-5. Table 4-8 lists specific organic compounds of interest, also referenced in Tables 4-4 through 4-6.

Tables 4-4 through 4-6 define the total data base that might be considered. Sections 4.2 and 4.3 present alternative phasing options for developing this total data base. Most of these phasing approaches call for monitoring the total data base only during an initial limited period (Phase 1). Monitoring conducted after that initial period would generally be a much-reduced (Phase 2) effort. For example, Phase 2 might consist of monitoring a limited number of "indicators" which "track" the entire data base. Therefore, in considering the monitoring suggestions in Tables 4-4 through 4-6, the monitoring plan developer should keep in mind that monitoring for the total data base need not be conducted indefinitely.

TABLE 4-4. DATA BASE SUGGESTIONS FOR GASEOUS DISCHARGE STREAMS

Generic Stream Category	Monitoring Suggestions[a]		Comments
	Survey Analytical Techniques[b]	Specific Component Suggestions	
1. Boiler/furnace flue gases from the combustion of conventional fuels		Criteria pollutants (see note c)	These streams are major potential sources of emissions in most synfuels facilities. However, these streams are not unique to synfuels plants. Monitoring is intended to be consistent with typical permits for flue gases from conventional sources such as fossil-fuel fired steam generators.
2. Boiler, furnace, or incinerator flue gases from combustion of process-derived fuels or wastes	Analysis for trace elements, e.g. ICP Analysis for aliphatics and aromatics, e.g. TCO/GRAV, GC/MS Analysis for nitrogenous compounds, e.g. GC/MS, GC-N specific	Criteria pollutants (see note c) Total Hydrocarbons (see note g) Reduced sulfur species (see note d) Reduced nitrogen species (see note e) Volatile trace elements (see note f) Organics in Table 4-8	Monitoring includes those parameters found in conventional flue gases, (i.e., criteria pollutants), plus monitoring to determine the degree of destruction of synfuel-derived pollutants in the feed. Parameter selection should be influenced by the composition of the feed, e.g., flue gases from combustion of a sulfur-free feed would not be monitored for sulfur species. Monitoring the feed for trace elements may be more convenient than monitoring the flue gases. Monitoring for organics should vary depending upon the source of the combustor feed. Some feed streams will be derived from essentially organic-free environments; others from organic-laden environments. Flue gases from fuel gas- or synthetic distillate-fired furnaces might not warrant detailed organics analysis unless initial screening analyses for total vapor phase hydrocarbons give high results. Off gases from tar-fired furnaces or sludge incinerators might suggest a greater need for detailed organics analyses.

(continued)

TABLE 4-4. (continued)

Generic Stream Category	Monitoring Suggestions[a]		Comments
	Survey Analytical Techniques[b]	Specific Component Suggestions	
3. Uncombusted vent gases or feed gases to flares.	Analysis for trace elements, e.g. ICP Analysis for aliphatics, aromatics and oxygenates, e.g. TCO/GRAV, GC/MS Analysis for nitrogenous compounds, e.g. GC/MS, GC-N specific Analysis for sulfur containing compounds, e.g. GC/MS, GC-S specific	Criteria pollutants (see note c) Total Hydrocarbons (see note g) Reduced sulfur species (see note d) Reduced nitrogen species (see note e) Volatile trace elements (see note f) Organics in Table 4-8	Monitoring of flare feeds is suggested due to the difficulty in monitoring flare combustion products and to identify potential components for ambient monitoring. Many flaring events will be intermittent and of short duration, and source monitoring may not be practical. Monitoring the source of the flare feed may be considered (i.e., monitor the source when it is not being flared). Flow rate data on flare feeds during flaring should be obtained if practical. Organics monitoring should vary depending on the feed source. Some feeds are essentially organic-free.
4. Tank vents	Analysis for aliphatics, aromatics and oxygenates, e.g. TCO/GRAV, GC/MS	Reduced sulfur species (see note d) Reduced nitrogen species (see note e) Total hydrocarbons (see note g) Organics in Table 4-8	Monitoring is intended to identify volatile components. Process vessels and product/by-product tankage containing unstabilized or unhydrotreated liquids may produce vent gases containing a wide variety of components. Monitoring selections should consider the characteristics of the fluids contained in the tank(s).
5. Process fugitive emissions	Analysis for aliphatics, aromatics and oxygenates, e.g. TCO/GRAV, GC/MS	Total hydrocarbons (see note g) Carbon monoxide H_2S NH_3	Any component in the fluids being processed can be released as a fugitive emission. The species suggested are intended as indicators of fugitive leaks. This information, along with composition of the fluid being processed, allows approximate levels of nonmonitored species to be estimated. Repeated high results for hydrocarbon measurements might trigger detailed organics analyses.

(continued)

TABLE 4-4. (continued)

Generic Stream Category	Monitoring Suggestions[a] Survey Analytical Techniques[b]	Monitoring Suggestions[a] Specific Component Suggestions	Comments
6. Fugitive emissions from waste impoundments, storage, or disposal facilities		Total Hydrocarbons Particulates H_2S	Off-site ambient monitoring may be the preferred approach in many cases. In some cases, depending on site design and on the wastes/materials stored in impoundments, hi-vol samplers might be placed on-site around the impoundment or the downwind transect method might be used. Characterization of feedstreams to the impoundment is suggested to identify potential components of fugitive emissions.
7. Fugitive particulate emissions		Particulates	Ambient monitoring for fugitive particulates will be the preferred approach in many cases. In some cases, on-site monitoring of suspended particulate from fugitive sources using hi-vol samplers might be desirable, depending on the location of off-site ambient monitors and the nature/significance of the fugitive particulates.

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[a] Flow rates and temperatures should also be measured for each point source discharge. Key process data should also be collected as necessary for interpretation of results; in particular, coal/oil shale/tar sand feed rate to the plant, feedstock composition, fuel burned in multi-fuel boilers nature and flow rate of uncombusted vent gases or flare feeds, nature of liquids contained in vented storage tanks, and nature of liquids/gases in process components potentially contributing to fugitive emissions should be noted or measured.

[b] For each entry in this column, a specific representative survey procedure is presented in Table 4-24 (Section 4.4) which would be applicable in most cases. Alternative procedures are listed in Table 4-27. When using these or the alternative techniques in Table 4-27, the extent of compound specific identification and quantification achievable at a reasonable cost is dependent on sample complexity and on the specific protocol used (e.g. sample volume). The indicated analyses should be performed on both vapor phase (volatile) samples and entrained particulates.
ICP = Inductively Coupled Optical Emission Spectrometry
GC/MS = Gas Chromatography/Mass Spectrometry
GC-N specific = Gas Chromatography with Nitrogen specific detection
GC-S specific = Gas Chromatography with Sulfur specific detection

[c] Criteria pollutants include SO_2, NO_x, CO, particulates, ozone and lead.

[d] Reduced sulfur species include H_2S, COS, CS_2, and mercaptans.

[e] Reduced nitrogen species include NH_3 and HCN.

[f] Volatile trace elements include antimony, arsenic, mercury, and selenium.

[g] Vapor phase, noncondensable hydrocarbons.

TABLE 4-5. DATA BASE SUGGESTIONS FOR AQUEOUS DISCHARGE STREAMS

Generic Stream Category	Monitoring Suggestions[a]		Comments
	Survey Analytical Techniques[b]	Specific Component Suggestions	
1. Wastewaters discharged to outfalls, impoundments or deep wells that are not unique to synfuels plants and have their origins in an organic-laden environment.	Analysis for trace elements, e.g. ICP Analysis for aliphatics and aromatics, e.g. TCO/GRAV, GC/MS	Water Quality Parameters (see Table 4-7)	Water quality parameters suggested for monitoring are intended to be consistent with monitoring in typical permits for similar streams in related industries.
2. Wastewaters discharged to outfalls, impoundments or deep wells that are not unique to synfuels plants, and have their origins in an organic-lean environment.	Analysis for trace elements, e.g. ICP	Water Quality Parameters (see Table 4-7)	Water quality parameters suggested for monitoring are intended to be consistent with monitoring in typical permits for similar streams in related industries.
3. Wastewaters codisposed with solid wastes or discharged to outfalls, impoundments or deep wells that result from the quenching, cooling, purifying, upgrading, etc. of the plant's main products.	Analysis for trace elements, e.g. ICP	Water Quality Parameters (see Table 4-7)	Monitoring is intended to identify potential organic and inorganic contaminants. Organic monitoring should reflect the characteristics of the raw wastewaters, e.g. high temperature gasification produces wastewater containing few organics while low or medium temperature gasification produces wastewaters high in organics. Organics monitoring for a treated discharge should reflect the level of organics in the raw wastewaters.
	Analysis for aliphatics, aromatics and oxygenates, e.g. TCO/GRAV, GC/MS	Volatile Trace Elements (see note c)	
	Analysis for nitrogenous compounds, e.g. GC/MS, GC-N specific on base/neutral extract.	Organics in Table 4-8	
	Analysis for sulfur containing compounds, e.g. GC/MS, GC-S specific		
	Biological screening tests		

(Continued)

TABLE 4-5. (continued)

	Monitoring Suggestions[a]		
Generic Stream Category	Survey Analytical Techniques[b]	Specific Component Suggestions	Comments
4. Wastewaters codisposed with solid wastes or discharged to outfalls, impoundments or deep wells that are unique to synfuels facilities but not included in category 3.	Analysis for trace elements, e.g. ICP	Water Quality Parameters (see Table 4-7)	Organics monitoring is intended to confirm the absence or near absence of organics in these discharges.
	Analysis for aliphatics and aromatics, e.g. TCO/GRAV, GC/MS	Volatile Trace Elements (see note c)	
	Biological screening tests	Organics in Table 4-8	

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[a] If streams from more than one category are combined, monitoring for the combined discharge should include the procedures suggested for each category present. Flow rates should also be measured for each discharge to an outfall, impoundment or deep well. Key process data should also be collected as necessary for interpretation of results; in particular, coal/oil shale/tar sand feed rate to the plant, feedstock composition, or special operating conditions of wastewater treatment systems (e.g., one unit in system malfunctioning) should be noted.

[b] For each entry in this column, a specific, representative survey procedure is presented in Table 4-25 (Section 4-4) which should be applicable in most cases. Alternative procedures are listed in Table 4-28. When using these or the alternative techniques in Table 4-28, the extent of compound specific identification and quantification achieveable at a reasonable cost is dependent on sample complexity and the specific protocol used (e.g. sample volume).

ICP = Inductively Coupled Optical Emission Spectrometry
GC/MS = Gas Chromatography/Mass Spectrometry
GC-N specific = Gas Chromatography with Nitrogen specific detection
GC-S specific = Gas Chromatography with Sulfur specific detection

[c] Volatile trace elements include antimony, arsenic, mercury, and selenium.

TABLE 4-6. DATA BASE SUGGESTIONS FOR SOLID DISCHARGES

	Monitoring Suggestions[d]		
Generic Stream Category	Survey Analytical Techniques[a]	Specific Component Suggestions	Comments
1. Organic-laden solid wastes not unique to synfuels plants.	Analysis for trace elements, e.g. ICP (whole sample and leachate) Analysis for leachable aliphatics and aromatics, e.g. TCO/GRAV, GC/MS[b]	Ultimate and proximate RCRA hazardous waste tests[c] Particle Size Radioactivity	Monitoring in categories 1 and 2 is intended to characterize the physical and chemical properties of the wastes and to identify potentially leachable constituents. The difference in monitoring is the inclusion of leachable organics in Category 1. The main purposes of these recommendations are to satisfy regulatory (e.g. RCRA) constraints and to confirm that these wastes are not unique to synfuels facilities. All monitoring suggestions are not practical for each stream type within the generic category. Judgment should be exercised in selecting analyses for each stream.
2. Organic-free or organic-lean solid wastes not unique to synfuels plants.	Analysis for trace elements, e.g. ICP (whole sample and leachate)	Ultimate and proximate RCRA hazardous waste tests[c] Particle Size Radioactivity	
3. Organic-laden solid wastes unique to synfuels plants	Analysis for trace elements, e.g. ICP (whole sample and leachate) Analysis for leachable and extractable aliphatics, aromatics and oxygenates, e.g. TCO/GRAV, GC/MS[b] Analysis for leachable and extractable nitrogenous compounds, e.g. GC/MS, GC-N specific[b] Analysis for leachable and extractable sulfur containing compounds, e.g. GC/MS, GC-S specific[b]	Ultimate and proximate RCRA hazardous waste tests[c] Particle Size Radioactivity TOC, COD in leachate	Monitoring in categories 3 and 4 is intended to characterize physical and chemical properties and to identify the constituents which could be atmospheric emissions (e.g. entrained particulates) or enter surface water or groundwater as leachates. The difference in monitoring is the level of organics for category 3. All monitoring suggestions are not practical for each stream type within the generic category. Judgment should be exercised in selecting the analyses for each stream.

(Continued)

TABLE 4-6. (continued)

Generic Stream Category	Monitoring Suggestions[d]		Comments
	Survey Analytical Techniques[a]	Specific Component Suggestions	
4. Organic-free or organic-lean solid wastes unique to synfuels plants.	Analysis for trace elements, e.g. ICP (whole sample and leachate) Analysis for extractable aliphatics and aromatics, e.g. TCO/GRAV, GC/MS	Ultimate and proximate RCRA hazardous waste tests[c] Particle Size Radioactivity TOC, COD in leachate	See comments for stream Category 3.

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[a] For each entry in this column, a specific, representative survey procedure is presented in Table 4-26 (Section 4.4) which should be applicable in most cases. Alternative procedures are listed in Table 4-29. When using these or the alternative techniques in Table 4-29, the extent of compound specific identification and quantification achievable at a reasonable cost is dependent on sample complexity and the specific protocol used (e.g., sample volume).
ICP = Inductively Coupled Optical Emission Spectrometry
GC/MS = Gas Chromatography/Mass Spectrometry
GC-N specific = Gas Chromatography with Nitrogen specific detection
GC-S specific = Gas Chromatography with Sulfur specific detection

[b] These analyses are suggested for leachates produced by neutral aqueous extraction and extracts produced using methylene chloride or other suitable organic extractant.

[c] Includes tests for toxicity and, where appropriate, ignitability, corrosivity, and reactivity.

[d] Monitoring should include measurement of flow rates of discharge streams. Key process data should also be collected as necessary for interpretation of results; in particular, coal/oil shale/tar sand feed rate to the plant, feedstock compositions, and any special operating features of solid waste generators (e.g. gasifier operating atypically) should also be noted.

TABLE 4-7. WATER QUALITY PARAMETERS OF INTEREST IN SYNFUELS WASTEWATERS[a]

pH
Color
Acidity
Alkalinity
Conductivity
Total solids
Settleable solids
TSS
TDS
COD
TOC
BOD_5
Phenols
Oil and Grease
Ammonia (total)
Cyanides
Formates
Thiocyanates
Sulfides
Sulfites
Sulfates
Chlorides
Fluorides
NO_2^-/NO_3^-
Phosphorus (total)
Radioactivity (gross α and β)
Dissolved oxygen
Chromium VI

[a] Depending on the composition of the wastewater being analyzed, some of these parameters will be of more interest than others.

TABLE 4-8. ORGANIC SPECIES OF SPECIAL INTEREST IN SYNFUELS DISCHARGE STREAMS

	Reasons for Special Interest[a]		
Species	Regulation, Guideline or Standard in Related Industry[b] or Contained on Pollutant List[c]	Toxic Properties, Health Effects, (References)[d]	Comments[e]
Benzene	NESHAP OSHA, Water Quality, Priority, RCRA VIII	Acute and chronic poison causing blood disorders (leukemia) in exposed workers and chromosomal aberrations (23, 24, 25 26, 27, 28)	Found in test data, potential indicator for simple aromatics.
Aniline	OSHA	Cases of acute and chronic poisoning reported, impairs oxygen transport ability (23, 24, 25, 29)	Found in test data, potential indicator for amines.
Anthracene/ phenanthrene	OSHA, Water Quality, Priority	May be present in soot, coal-tar, and pitch, which are known to be carcinogenic to man (23, 25, 30)	Found in test data, potential indicator for higher weight polycyclics

(Continued)

TABLE 4-8. (continued)

	Reasons for Special Interest[a]		
Species	Regulation, Guideline or Standard in Related Industry[b] or Contained on Pollutant List[c]	Toxic Properties, Health Effects, (References)[d]	Comments[e]
Phenol	OSHA, Water Quality, EGD-refining and coking, NESHAP*, Priority, RCRA VIII	Acute and chronic poisoning, causing damage to liver and kidneys (23, 24, 26)	Found in test data, potential indicator for oxygenates
Pyridine	OSHA, RCRA VIII	Skin irritant, causes depression of central nervous system, chronic poisoning causes damage to liver, kidney and bone marrow (23, 25)	Found in test data, potential indicator for nitrogen-containing heterocyclics
Benzopyrene	Water Quality, Priority, RCRA VIII	Active carcinogen, causes chromosomal aberrations in mammalian cells (23, 24, 31)	Found in test data, potential indicator for higher weight polycyclics

[a] Compounds on this list are included because they are generally accepted as toxic and hazardous compounds and/or are possible indicators of the potential presence of similar compounds which are toxic and hazardous.

[b] NAAQS = National ambient air quality standards
NESHAP = National emissions standards for hazardous air pollutants
OSHA = OSHA toxic and hazardous air contaminants
Water Quality = Water Quality Criteria
EGD-refining = Effluent Guidelines for petroleum refining
EGD-coking = Effluent Guidelines for byproduct coking

[c] NESHAP* = Compounds considered for regulations under NESHAP
Priority = Priority pollutants (NRDC vs. EPA)
RCRA VIII = RCRA Appendix VIII hazardous constituents

[d] Numbers refer to references in Section 4.5. For example, if 23 is shown, it indicates reference 4-23.

[e] For a full listing of compounds of concern for which these species may be indicators, see Table 4-20.

Some of the data needs suggested in Tables 4-4 through 4-6 will be satisfied by permit-required monitoring, depending on the requirements for a specific plant. The discharge streams actually monitored at a specific plant will depend on the design and circumstances of the plant. (Not all of the streams in Tables 4-4 through 4-6 would have to be monitored at every plant.) Not all of the monitoring suggestions are applicable to all streams in a generic stream category. In addition, some plants might have multiple discharges of the same type (e.g., vents from three product gasoline storage tanks). In such cases, only one of the identical multiple discharges would have to be monitored to supply data base needs.

Tables 4-4 through 4-6 suggest three types of monitoring: (1) "survey" analyses that can detect many species in a single sample (e.g. analysis for aliphatics and aromatics via gas chromatography/mass spectrometry); (2) sampling and analysis for a specific chemical component or tests for a specific property (e.g. analysis of H_2S in uncombusted vent gases); and (3) biological testing (included under the "survey analytical techniques" heading).

Monitoring suggestions of the first type ("survey" analytical techniques) are emphasized as an effective means of screening for substances actually present, without attempting to judge, *a priori*, which specific compounds will ultimately prove to be present. The application of survey techniques thus helps assure that the monitoring program is tailored to the needs of each individual site. If, in lieu of the survey procedures, a list of specific preselected compounds were developed for inclusion in all monitoring programs, there would be a risk that:

- some potentially significant compounds that are actually present at a specific facility might be missed, because they were not foreseen and not included on the list (this concern could result in any such list being conservatively long); and
- some compounds which are not actually present might be monitored repeatedly because they are on the list.

The classes of substances addressed by the survey techniques include trace organics and trace metals. For these classes the operator of the monitoring program would be likely to use the suggested survey procedures, even if focusing on a pre-selected list. Therefore, the application of survey techniques seems to offer a technically sound and cost-effective approach.

The intent of the survey technique approach is to limit the suggested techniques to a few well-defined procedures that provide the maximum amount of information at reasonable cost. As shown in Tables 4-4 through 4-6, representative survey techniques include, for example, gas chromatography/mass spectrometry for trace organics analysis, and inductively-coupled optical emission spectrometry for trace elements. These specific, representative procedures--defined further in Section 4.4 (Tables 4-24 through 4-26)--can detect many substances. However, in some cases, matrix effects and/or the aggregate level of contaminants in a given sample could mask the presence, or give erroneous quantitation, of some compounds which could be accurately detected otherwise. For these and other reasons, it might be desirable to select one of the alternatives to the survey procedures, listed in Tables 4-27 through 4-29.

Monitoring suggestions of the second type in Tables 4-4 through 4-6 (analysis for a specific component or property) include:

- monitoring for substances which are regulated (e.g., criteria air pollutants, RCRA hazardous waste tests) and substances which, if not always covered by some discharge or ambient quality standard, are conventionally included for monitoring in many permits (e.g., H_2S, NH_3, some of the water quality parameters); and
- monitoring for organic species of particular interest (Table 4-8); these organics are included because they are generally recognized as toxic and/or are potential indicators of similar compounds which are toxic.

Most of the organics listed in Table 4-8 will normally be detected using the survey analytical techniques. In cases where the substances in Table 4-8 are effectively quantified by the survey procedures, further analyses are unnecessary. However, where a particular sample does not permit the determination of one or more of these substances using the survey techniques (e.g., due to interferences), then alternative analytical techniques aimed specifically at the pertinent substances are suggested.

The third type of monitoring suggested in Tables 4-4 through 4-6 is biological testing. It is suggested only for the two generic wastewater categories which include streams unique to synfuels facilities. The use of biological testing to identify discharge streams having possible unique (and potentially hazardous) impacts can provide perspectives beyond those derived from chemical testing. Biological tests are probably most useful in defining relative impacts of discharge streams and in detecting possible synergistic or antagonistic matrix effects. Some typical biological screening tests employed for these purposes are listed in Table 4-9. Impacts of discharges on aquatic ecology can be defined using test organisms representative of those indigenous to the receiving water (e.g., minnows or daphnia) in a phased biomonitoring program. A typical test sequence might include (1) one or more acute toxicity screening tests in undiluted effluent and one or more mutagenicity screening tests, (2) 96-hour flow through tests for effluents identified as toxic in (1) using minnows to determine LC_{50}, (3) bioaccumulation tests to determine chemical uptake over a specified time period, and (4) short-term chronic toxicity tests.

A fourth type of monitoring or data gathering not explicitly suggested in Tables 4-4 through 4-6 is plant operating data such as unit feed rates, product output rates, or process temperatures. Such measurements are of course necessary to allow emission rates to be calculated and to allow proper assessment of plant operating status during the monitoring effort. Suggested monitoring for plant operating parameters is discussed further in Section 4.1.3.

TABLE 4-9. COMMONLY USED TECHNIQUES FOR DETERMINING THE BIOLOGICAL ACTIVITY OF SPECIFIC WASTE STREAMS

Test Objective	Test Designation	Activity Measured	Test Organism
Health Effects			
Cellular (in-vitro)	Ames	Mutagenesis (point mutation)	Salmonella Typhimurium
	RAM	Cytotoxicity EC_{50}	Rabbit Alveolar Macrophage
	CHO	Cytotoxicity EC_{50}	Chinese Hamster Ovary
	CHO/K1	Mutagenesis (point mutation)	Chinese Hamster Ovary (K1 cell line)
	CHO/SCE*	Mutagenesis (gross genetic change)	Chinese Hamster Ovary
Aquatic Ecology			
Whole Animal (Vertebrate)	Acute Static Bioassay (48 or 96 hr)	Lethality, LC_{50}	Fresh Water or Marine Minnow
Whole Animal (Invertebrate)	Acute Static Bioassay (48 or 96 hr)	Lethality, EC_{50} Lethality, EC_{50}	Daphnia (fresh water) or Shrimp (marine)
Algal	Algal growth	Growth Inhibition, EC_{50}	Algae: Selenastrum capricornutum (fresh water) Skeletonema costatum (marine)

*Sister chromatid exchange

In order to select appropriate survey techniques to develop the data base for organics and trace elements, a number of data sources were reviewed to identify substances of interest in synfuels waste streams. These sources included:

- regulations, standards, and criteria for similar discharge streams from related industries,
- lists of known pollutants, and
- synfuels test data.

The results of this review are summarized in Tables 4-10 (for organic compounds/classes) and Table 4-11 (for trace elements). For each compound or class, references are provided to show the specific regulations, pollutant lists or test data which support the inclusion of the substance in the tables.

Under most circumstances, the few survey techniques suggested in Tables 4-4 through 4-6 (and further defined in Tables 4-24 through 4-26) should detect most of the substances listed in Tables 4-10 and 4-11, plus other unlisted substances in the same groups. The substances listed in these tables might be considered as some of those to which the analyst might be alert when interpreting the results of survey techniques. The tables should not be construed as a list of the substances that must be individually determined during monitoring, nor as a comprehensive listing of the only substances that need to be considered. If approaches other than the suggested survey techniques are proposed in a monitoring plan, attention should be given to how well the different approach would address the substances in Tables 4-10 and 4-11.

The organics in Table 4-10 belong to one of five chemical groups, based on their dominant functional characteristic.

- aliphatics
- aromatics
  - simple aromatics (benzene/toluene/xylene)
  - polynuclear aromatics (PNAs)

TABLE 4-10. ORGANIC SUBSTANCES OF INTEREST IN SYNFUELS WASTE STREAMS[a]

Compound	CAS Registry Number[b]	Reason for Interest: Regulation, Guideline or Standard Exists in Related Industry[c,d]	Reason for Interest: Contained on Pollutant List[d,e]	Reason for Interest: Found in Synfuels Test Data[d,f]
Aliphatics				
alkanes	00074-82-8	OSHA		1,2,5,6,7
cycloalkanes		OSHA, FWPCA		1,2,8
alkenes	00074-85-1	OSHA, FWPCA		1,2,8
alkadienes		OSHA	RCRA VIII, PWC	1,2,8
Aromatics				
Simple Aromatics				
benzene	00071-43-2	OSHA, Water Quality, FWPCA	Priority, RCRA VIII TSCAR	1,2,4,6,12,13
toluene	00108-88-3	OSHA, Water Quality, FWPCA	NESHAP*, Priority, RCRA VIII, TSCAR	1,2,4,6,12,13
alkyl benzenes		OSHA, Water Quality, FWPCA	NESHAP*, Priority, RCRA VIII, TSCAR	1,2,4,6,8,12,13
biphenyls	00092-52-4	OSHA	PWC	2,8,12
indans/indenes	00496-11-7/ 00095-13-6	OSHA, Water Quality	Priority	1,2,4,13
Polynuclear Aromatics				
naphthalenes	00091-20-3	OSHA, Water Quality, FWPCA	Priority, RCRA VIII	1,2,4,5,8,12
anthracenes/phenanthrenes	00120-12-7/ 00085-01-8	OSHA, Water Quality	Priority	1,2,4,13
acenaphthenes	00083-32-9	Water Quality	Priority	2,12
acenaphthylenes	00208-96-8		Priority	4,5,13
benz(a)anthracenes	00056-55-3	Water Quality	Priority, RCRA VIII	2,6
pyrenes/chrysenes	00129-00-0/ 00218-01-09	Water Quality	Priority, RCRA VIII	1,2,4,13
benzopyrenes		Water Quality	Priority, RCRA VIII	2,4
dibenzanthracenes		Water Quality	Priority, RCRA VIII	6
benzoperylenes		Water Quality	Priority	5
dibenzoperylenes		Water Quality		
fluorenes	00086-73-7	Water Quality	Priority	1,2,4,12
fluoranthenes	00206-44-0	Water Quality	Priority, RCRA VIII	1,2,4,13
benzofluoranthenes		Water Quality	Priority, RCRA VIII	4,14
indenopyrenes		Water Quality	Priority	
cholanthrenes		Water Quality	RCRA VIII	6
Nitrogenous Compounds				
Amines and Heterocycles				
alkyl amines/diamines		OSHA, FWPCA	RCRA VIII	
aniline	00062-53-3	OSHA, FWPCA	RCRA VIII	1,2,5,8,11,12
alkylanilines		OSHA		2,5,8
naphthyl amines			RCRA VIII	5
aromatic diamines		OSHA	RCRA VIII	
aminobiphenyls			Priority, RCRA VIII, TSCAR	
aromatic amines				5
pyridines	00110-86-1	OSHA	RCRA VIII	1,2,4,5,6,7,8,10,11,12
pyrroles	00109-97-7			1,2,5,8,12
indoles	00120-72-9			1,2,4,5,8,12
carbazoles	00086-74-8		RCRA VIII	2
quinolines	00091-22-5	FWPCA		2,4,5,6,8,12
acridines	00260-94-6		RCRA VIII	2
morpholines	00110-91-8	OSHA		

(Continued)

TABLE 4-10. (continued)

Compound	CAS Registry Number[b]	Reason for Interest: Regulation, Guideline or Standard Exists in Related Industry[c,d]	Reason for Interest: Contained on Pollutant List[d,e]	Reason for Interest: Found in Synfuels Test Data[d,f]
Nitrogenous Compounds (continued)				
Nitriles/Isocyanates				
alkyl nitriles	00075-05-8	OSHA	NESHAP*, Priority, RCRA VIII	1,12,13
aromatic nitriles	00100-47-0	FWPCA		8,12
alkyl isocyanates	00624-83-9	OSHA		
aromatic diisocyanates		OSHA		
Oxygenates				
Phenolics				
phenol	00108-95-2	OSHA, Water Quality, EGD-refining, EGD-coking, FWPCA	NESHAP*, Priority, RCRA VIII	1,2,3,4,5,6,8,9,10,11,12,13
alkyl phenols		OSHA, FWPCA	NESHAP*, Priority, RCRA VIII, TSCAR	1,2,4,5,6,8,9,10,11,12,13
naphthols				1,2,4,5,8,10
dihydric phenols		OSHA, FWPCA	RCRA VIII	2,4,5,10
indanols/indenols				4,5,8,10
benzofuranols				10
Carboxylic Acids				
alkyl acids	00064-18-6	OSHA, FWPCA	RCRA VIII	1,2,9,10,11,12
aromatic acids	00065-85-0			5
Other Oxygenates				
alkyl ethers	00115-10-6	OSHA		1
dioxanes		OSHA	NESHAP*, RCRA VIII	1
aromatic ethers		OSHA		12
alkyl alcohols	00067-56-1	OSHA	RCRA VIII	2,5
cyclo alcohols		OSHA		1
cellosolves		OSHA		
alkyl ketones	00067-64-1	OSHA	RCRA VIII, PWC	1,8,10,12,13
cyclo ketones		OSHA	RCRA VIII, Priority, TSCAR	8,12
aromatic ketones	00098-86-2	OSHA	RCRA VIII	
alkyl aldehydes	00050-00-6	OSHA, FWPCA	NESHAP*, RCRA VIII, TSCAR	12,13
aromatic aldehydes	00100-52-7			12
alkyl esters	00079-20-9	OSHA, FWPCA	RCRA VIII	5
aromatic esters	00093-58-3			12
phthalate esters	00131-11-3	OSHA, Water Quality, FWPCA	Priority, RCRA VIII	2,4,5
furans	00110-00-9		RCRA VIII	1,2,8,12
benzofurans	00271-89-6			1,2,12
dibenzofurans	00132-64-9		PWC	1,2,12

(Continued)

TABLE 4-10. (continued)

Compound	CAS Registry Number[b]	Reason for Interest: Regulation, Guideline or Standard Exists in Related Industry[c,d]	Reason for Interest: Contained on Pollutant List[d,e]	Reason for Interest: Found in Synfuels Test Data[d,f]
Sulfur Containing Compounds				
alkyl mercaptans		PSD, OSHA, FWPCA	RCRA VIII	1,6,7
alkyl disulfides		PSD, OSHA		1,2
thiophenes	00110-02-1			1,7,8,12
benzothiophenes	00095-15-8			1,2,8,12

[a] This table should not be construed as a list of organic substances that must be determined individually by monitoring, nor should it be construed as a comprehensive list of all the substances that need be considered. Rather, it is a suggestion of some substances an analyst might be alert to when interpreting results of survey analytical techniques. Survey analytical techniques are presented in Tables 4-4 tnrough 4-6 and Tables 4-24 through 4-26 in Section 4.4.

[b] Chemical Abstract Service (CAS) numbers are for the parent compound (e.g. the CAS number shown for alkyl alcohols is for methanol although the term alkyl alcohols is intended to include all alkyl alcohols. CAS numbers are not provided for entries where tne parent compound is not straightforward (e.g. benzopyrenes).

[c] NESHAP = National emissions standards for hazardous air pollutants (Section 112 of Clean Air Act)
PSD = Pollutants for which de minimis values exist (may be part of a general class of compounds) relating to prevention of significant deterioration regulations
OSHA = OSHA toxic and hazardous air contaminants
Water Quality = Pollutants for which water quality criteria have been developed by EPA pursuant to Section 304 of the Clean Water Act
EGD-refining = Effluent Guidelines for petroleum refining
EGD-coking = Effluent Guidelines for byproduct coking
FWPCA = Pollutants addressed by Section 311 (Oil and Hazardous Substance Liability) of the Federal Water Pollution Control Act

[d] Some of the classes of compounds listed in this table include a number of single specific compounds, e.g., alkylbenzenes includes ethylbenzene, propyl benzene, isopropyl benzene, and the butyl benzenes. When a regulation, standard, pollutant list, or test data source is cited for such a class, it means that one or more members of the class but not all members are covered by the regulation, standard, or list.

[e] NESHAP* = Compounds considered for regulations under NESHAP (Section 112 of Clean Air Act)
Priority = Priority pollutants (NRDC vs. EPA)
RCRA VIII = RCRA Appendix VIII hazardous constituents
PWC = Pollutants under consideration for development of water quality criteria pursuant to Section 304 of tne Clean Water Act
TSCAR = Toxic Substances Control Act Review - committee to review compounds for possible EPA testing

[f] Numbers refer to references in Section 4.5. For example, if 13 is shown, it indicates data are from reference 4-13.

TABLE 4-11. TRACE ELEMENTS OF INTEREST IN SYNFUELS WASTE STREAMS[a]

Trace Element[b]	CAS Registry Number[c]	Reason for Interest		
		Regulation, guideline or standard exists in related industry[d]	Contained on Pollutant List[e]	Found in Synfuels Test Data[f]
Antimony	07440-36-0	OSHA, FWPCA	Priority, RCRA VIII, TSCAR	2,7,9,13,17,19,21
Arsenic	07440-38-2	OSHA, Water Quality, FWPCA Drinking Water, RCRA EP	Priority, RCRA VIII RPAR, TSCAR	1,2,6,7,13,14,15,16,17,18,19,20 21,22
Barium	07440-39-3	OSHA, Water Quality, FWPCA Drinking Water,RCRA EP	Priority, RCRA VIII, PWC	1,2,7,13,14,15,16,17,18,19,22
Beryllium	07440-41-7	NESHAP, PSD, OSHA, Water Quality, FWPCA	Priority, RCRA VIII	13
Boron	07440-42-8	Water Quality	PWC	1,2,7,13,14,15,16,17,18,19,20,22
Cadmium	07440-43-9	OSHA, Water Quality, Drinking Water, RCRA EP, FWPCA	Priority, RCRA VIII, RPAR, TSCAR	3,6,7,13,15,18,19,22
Chlorine	07782-50-5	OSHA, Water Quality, Drinking Water, EGD-steam, FWPCA	PWC, RCRA VIII, TSCAR	1,2,3,6,7,13,15,16,17,18
Chromium	07440-47-3	OSHA, Water Quality, Drinking Water, EGD-refining, EGD-steam, RCRA EP, FWPCA	Priority, RCRA VIII, TSCAR	1,6,13,14,15,16,17,18,19
Copper	07440-50-8	Water Quality, Drinking Water, EGD-steam, FWPCA	Priority RCRA VIII	1,2,3,6,7,13,15,16,17,18,19,21
Fluorine	07782-41-4	PSD, OSHA, Drinking Water, FWPCA	RCRA VIII, PWC	6,7,13,14,16,17,18,19
Iron	07439-89-6	Water Quality, Drinking Water EGD-steam, EGD-mining, FWPCA	RCRA VIII	1,2,3,7,13,15,16,17,18,19,20,21,22
Lead	07439-92-1	NAAQS, PSD, OSHA, Water Quality, Drinking Water, RCRA EP, FWPCA	Priority, RCRA VIII	3,6,13,15,16,17,18,19,22
Manganese	07439-96-5	OSHA, Water Quality, Drinking Water, EGD-mining, FWPCA	NESHAP*, PWC	1,2,13,14,15,16,17,18,19,21,22
Mercury	07439-97-6	NESHAP, PSD, OSHA, Water Quality, Drinking Water, RCRA EP, FWPCA	Priority, RCRA VIII, TSCAR	2,6,13,14,16,17,18,19,21
Molybdenum	07439-98-7	OSHA	PWC	3,13,17,18,19,20,21
Nickel	07440-02-0	OSHA, Water Quality, FWPCA	NESHAP*, Priority, RCRA VIII	1,3,6,13,14,15,16,17,18,19,21,22
Phosphorus	07723-14-0	EGD-steam, FWPCA	RCRA VIII, PWC	2,7,13,16,17,18
Selenium	07782-49-2	OSHA, Water Quality, Drinking Water, RCRA EP, FWPCA	Priority, RCRA VIII	1,2,6,7,13,14,15,16,17,18,19
Silver	07440-22-4	OSHA, Water Quality, Drinking Water, RCRA EP, FWPCA	Priority, RCRA VIII	1,7,13,15,18
Thallium	07440-28-0	OSHA, Water Quality, FWPCA	Priority, RCRA VIII	
Tin	07440-31-5	OSHA		7,13,15,17,18
Vanadium	07440-62-2	OSHA, FWPCA	RCRA VIII, PWC	2,13,15,18,19
Zinc	07440-66-6	Water Quality, Drinking Water, EGD-steam, FWPCA	RCRA VIII	1,2,3,6,13,14,15,16,17,18,19

(Continued)

TABLE 4-11. (continued)

[a] This table should be construed only as a suggestion of some of the substances an analyst might be alert to when interpreting results of the survey analytical techniques presented in Tables 4-4 through 4-6 and Tables 4-24 through 4-26 in Section 4.4

[b] Includes the total quantity of element present, i.e., both the free element and its compounds.

[c] Chemical Abstract Service Registry Number

[d] NAAQS = National ambient air quality standards
NESHAP = National emissions standards for hazardous air pollutants (Section 112 of Clean Air Act)
PSD = Pollutants for which de minimis values exist (may be part of a general class of compounds) relating to prevention of significant deterioration regulations
OSHA = OSHA toxic and hazardous air contaminants
Water Quality = Pollutants for which water quality criteria have been developed by EPA pursuant to Section 304 of the Clean Water Act
Drinking Water = Primary and Secondary Drinking Water Standard
EGD-refining = Effluent Guidelines for petroleum refining
EGD-steam = Effluent Guidlines for steam electric power generating
EGD-mining = Effluent Guidelines for coal mining
RCRA EP = RCRA Extraction Procedure for toxic pollutants
FWPCA = Federal Water Pollution Control Act Oil and Hazardous Substances listing for regulatory promulgation

[e] NESHAP* = Compounds considered for regulations under NESHAP (Section 112 of Clean Air Act)
Priority = Priority pollutants (NDRC vs. EPA)
RCRA VIII = RCRA Appendix VIII hazardous constituents
PWC = Pollutants under consideration for development of water quality criteria pursuant to Section 304 of the Clean Water Act
TSCAR = Toxic Substances Control Act Review - committee to review compounds for possible EPA testing
RPAR = Rebutable Presumption Against Registration (Subject to manufacturing, transporting and use restrictions.)

[f] Numbers refer to references in Section 4.5. For example, if 13 is shown, it indicates data found in reference 4-13.

- nitrogenous compounds
  - heterocycles and amines
  - nitriles and isocyanates
- oxygenates
  - phenols
  - carboxylic acids
  - other oxygenated compounds
- sulfur containing compounds

Over seventy compounds or classes of compounds are listed in Table 4-10. If each individual compound in each class were listed, the number of entries would be even greater. However, as indicated in Tables 4-4 through 4-6, only a few survey techniques are needed to identify the five groups of organic compounds in Table 4-10.

The regulations, standards, or criteria reviewed to develop the lists of organics and trace elements of interest included 1) non-source-specific documents such as national ambient air quality standards, the OSHA list of air contaminants, and water quality criteria, and 2) source-specific documents such as new source performance standards and effluent guidelines for related industries. Pollutant lists reviewed for substances of interest included the list of compounds considered for regulation under NESHAP, the priority pollutant list, and the RCRA Appendix VIII hazardous constituents list.

Table 4-10 is not a summary of all organic substances contained in the regulations, standards, criteria, and pollutant lists reviewed. Many of the substances found on those lists are not expected to be present in synfuels discharge streams, and accordingly, were not included. Most of the substances not included are manufactured chemicals or by-products of chemical manufacturing. For example, halogenated herbicides, pesticides, and insecticides--major components in the priority pollutant list for aqueous streams--are not likely to be present in synfuels waste streams and are not included in Table 4-10.

For the most part, the available synfuels test data referenced in Tables 4-10 and 4-11 were for raw waste streams and not treated discharges. The assumption could be made that many of the substances found in test data for raw waste streams would be either absent or present at very low or undetectable levels in treated discharges. However, this does not diminish the need to establish the presence or absence and, if necessary, the concentration of the substance in the treated discharge.

The synfuels test data review did not involve an exhaustive search of publicly available data. However, the data sources examined were adequate to identify the major classes of organics which could be present in synfuels discharge streams. In developing monitoring plans, synfuels facility developers are encouraged to use their own test data to supplement or modify the data base requirements identified in this manual.

4.1.3 Control Technology Monitoring

Control technology monitoring involves collection of data that define relationships between inlet stream characteristics, control device operating conditions and outlet stream characteristics. While the major objective of source monitoring is to characterize discharge streams, there are many benefits to be gained from monitoring and reporting data for the inlet streams to control devices and the operating conditions of those devices (in addition to data on the resulting discharge stream):

- Synthetic fuel process developers and environmental agencies would be better able to assess the performance of applied control devices, thus improving the chances for mitigating potential problems in future facilities. This assessment would include an evaluation of the performance of the device in removing both regulated and unregulated species.
- The data would provide insight into control device performance problems and allow identification of control technology design improvements and development needs for future facilities.

- Facility operators might be able to reduce Phase 2 monitoring costs by monitoring easy-to-monitor inlet stream characteristics and/or certain operating conditions instead of discharge stream characteristics. Of course, a good correlation between inlet stream compositions, operating condition(s), and discharge stream compositions would be required to implement this approach.

In many cases, plant operators will routinely monitor control device inlet stream characteristics and operating conditions to control plant operations. If so, the collection and reporting of these results might not significantly increase monitoring expenses.

The strongest justification for the acquisition of control process performance data in addition to data on discharge stream characteristics is related to the primary objective of the source monitoring program itself, i.e., to avoid environmental problems identified in first generation facilities in future replications of the technologies. There is currently a somewhat limited understanding of design requirements, performance capabilities, and reliability of conventional control processes in a synthetic fuels plant application. Early identification of the sources of any control device performance problems will help assure that future controls can be designed for cost-effective and reliable performance.

In some cases, an interest in monitoring the inlet to a control device might be stimulated by pollutant levels monitored in the outlet. For example, high levels of organics in a control device outlet stream might make it desirable to check for variations in inlet stream composition or control device operating considerations to determine whether these factors were contributing to high output levels.

Collection of data on control device operating conditions and inlet stream composition might allow the development of simple performance models. Such model development and validation could benefit both the facility operator and environmental agencies. A data base would be provided for use in designing reliable controls and predicting performance of proposed controls. In addition, a facility operator might be able to demonstrate that emissions would be expected to remain within a defined range as long as certain gross inlet composition parameters (e.g., VOC and incinerator temperature) are in specified ranges.

While the benefits of control technology monitoring are readily apparent, site specific constraints might limit the ability of a plant owner to gather and/or report data on control device performance. These constraints include:

- Data on some internal stream properties or control device performance parameters may be proprietary.
- Key inlet stream properties may be significantly different (more complex matrix) or more highly variable than outlet stream properties, complicating the monitoring effort.
- In some cases, multiple control devices are linked in series to produce a treatment "train". In such cases, the resources required to monitor each individual control device in the series should be weighed against the value of the information gained by monitoring to determine whether monitoring every device is warranted.

The above factors suggest that control device monitoring program specifications must be established on a site specific basis.

Tables 4-12 through 4-14 are provided to aid in formulation of a control technology monitoring program for gaseous, aqueous and solid stream controls, respectively. These tables present:

- The major types of control devices that might be considered for synfuels facilities.
- The major substances controlled by each device and typical removal efficiencies. Inlet stream monitoring would logically include the same array of substances/survey techniques considered for the outlet stream (as listed in Tables 4-4 through 4-6), in order to provide a good data base for

TABLE 4-12. TYPICAL SYNFUELS PLANT CONTROL DEVICES AND KEY OPERATING VARIABLES--GASEOUS STREAMS

Stream Control Options	Substances Controlled[a]	Typical Uncontrolled Emissions Levels	Typical Outlet/ Control Levels	Secondary Discharge Streams	Major Control Device Operating Parameters Affecting Emission Levels[b]
Stream Type: Combustion Flue Gases (Generic Categories 1 and 2 in Table 4-1)					
Particulate Controls					
Baghouses	Particulates	Up to 10 lb/10^6 Btu (for coal-fired boilers)	<0.10 lb/10^6 Btu	Collected solids	Air/cloth ratio Bag cleaning procedures, Pressure drop
ESPs	Particulates	Up to 10 lb/10^6 Btu	<0.10 lb/10^6 Btu	Collected solids	Precipitation rate (function of particule resistivity, particle size distribution, gas velocity distribution, rapping frequency, electrical factors) Specific collection area (plate area) Gas flow rate Particulate loading
Wet Scrubbers	Particulates (potentially SO_2)	Up to 10 lb/10^6 Btu	<0.30 lb/10^6 Btu	Collected solids (wet) Liquid blowdown	Liquid-to-gas ratio Gas velocity Energy consumption Particle size distribution and loading
Mechanical Collectors (cyclones)	Particulates	Up to 10 lb/10^6 Btu	<1 lb/10^6 Btu	Collected solids	Inlet gas velocity (performance affected greatly by large load swings) Particle size distribution and loading

(Continued)

TABLE 4-12. (continued)

Stream Control Options	Substances Controlled[a]	Typical Uncontrolled Emissions Levels	Typical Outlet/ Control Levels	Secondary Discharge Streams	Major Control Device Operating Parameters Affecting Emission Levels[b]
Stream Type: Combustion Flue Gases (Generic Categories 1 and 2 in Table 4-1)					
SO_2 Controls					
Wet Scrubbers	SO_2 (potentially particulates)	Up to 10 lb/10^6 Btu	50-90+% removal	Calcium based sludge (from lime, limestone and dual alkali processes); or sulfur or H_2SO_4 (from regenerable systems such as Wellman-Lord); or aqueous wastes (high TDS blowdown streams from sodium-based scrubbing systems)	SO_2 inlet concentration Gas residence time Gas/liquid contact area Liquid-to-gas ratio Liquid phase alkalinity (key soluble species in liquid phase)
Spray Dryers	SO_2 (and particulates in downstream solids collection device)	Up to 10 lb/10^6 Btu	50-80% removal	Dry solids (sodium or calcium based salts and any particulate matter in the feed stream such as boiler fly ash)	SO_2 inlet concentration Sorbent type (sodium or calcium-based) and sorbent/SO_2 ratio Gas residence time Liquid-to-gas ratio Dryer outlet temperature Dry solids recycle
Fuel Pretreatment (e.g. desulfurized fuel gas)	H_2S, RSH, SO_2	N/A	Up to 90% removal	Rich acid gases or sulfur	Same as controls for AGR offgases (see below)
NO_x Controls					
Combustion Modifications (e.g. LEA, SC, FGR)	NO_x	<1 lb/10^6 Btu	10-50% reduction	Must be careful to control potential increases in CO, particulate, and HC emissions with combustion mods	Excess air, fuel N content OFA port location, Burner design Gas recirculation rate
Post Combustion Controls Ammonia injection Catalytic reduction	NO_x	<1 lb/10^6 Btu	40-80%	NH_4HSO_4 deposits on outlet duct and air preheater surfaces	NO_x inlet concentration NH_3 injection rate, mixing temperature Space velocity, catalyst activity, NH_3/NO_x ratio

(Continued)

TABLE 4-12. (continued)

Stream Control Options	Substances Controlled[a]	Typical Uncontrolled Emissions Levels	Typical Outlet/ Control Levels	Secondary Discharge Streams	Major Control Device Operating Parameters Affecting Emission Levels[b]
Stream Type: Sulfur Recovery System Offgases (Generic Category 3 in Table 4-1)					
Bulk Sulfur Recovery Processes					
Claus	H_2S RSH	5-20+% 100 ppm	90% total S	Spent catalyst Catalyst regeneration offgases Knockout drum condensate	H_2S concentration High CO_2 can adversely affect sulfur removal NH_3 and HC can cause catalyst pluggage and catalyst deactivation and affect sulfur removal HCN presence in feed gas can cause corrosion problems and catalyst deactivation
Stretford	H_2S HCN RSH	Up to 5% 100 ppm 100 ppm	<10 ppm >90% up to 90%	Oxidizer vent gas Purge solution Sulfur (if not produced at marketable quality)	High CO_2 will decrease absorption efficiencies Solvent recirculation rate Gas/liquid contact time Inlet H_2S concentration
Tail Gas Treatment Processes					
(e.g. Beavon, SCOT, Wellman-Lord)	Depends on process SO_2, H_2S, COS, RSH	<1% total sulfur	>90%	Depends on process S, spent catalyst blowdown solvent recovered acid gases	Process temperature, reactant/feed ratio, catalyst activities, solution regeneration efficiency
Stream Type: CO/Hydrocarbon Rich Streams (Generic Categories 3 and 4 in Table 4-1)					
Waste Gas Incinerators	VOC, red S/N, CO	Combustible gases	99+%	Flue gas	Excess air, temperature, residence time
Carbon Adsorption Units	VOC	Up to 2-5% HC	90+%	Spent carbon, carbon regeneration offgases	Temperature, regeneration efficiency, carbon loading, nature of organics

[a] Monitoring in the inlet stream to a control device could include the same substances/survey techniques considered for the outlet stream (Table 4-4). However, the emphasis for inlet stream monitoring might be placed on the major substances the device was designed to control.

[b] Control device operating parameters to be monitored might be chosen from this column.

TABLE 4-13. TYPICAL SYNFUELS PLANT CONTROL DEVICES AND KEY OPERATING VARIABLES--AQUEOUS STREAMS

Process	Substances Controlled[a]	Typical Control Efficiency	Secondary Discharge Streams	Major Control Device Operating Parameters Affecting Emission Levels[b]
Solvent Extraction	Phenols, TOC, COD, BOD	90+% phenolic compounds	Recovered phenols Spent filter media	Solvent type, S/W ratio, pH, temperature, equilibrium stages, recovery system operation
Biological Oxidation	BOD, TOC, some trace metals, specific organics	85+% BOD	Sludge Air emissions	Hydraulic residence time, sludge age, aeration rate, F/M ratio, sudden changes in influent composition
Carbon Adsorption	TOC, COD, some trace metals, specific organics	80+%	Spent carbon Carbon regeneration offgases Backwash stream	Nature of pollutants present, temperature, pH, contact time, regeneration efficiency
Chemical Oxidation	COD, TOC, $S^=$, CN^-, NH_3, specific organics	80+%	Sludge Evolved gases	Oxidant/feed ratio, temperature, residence time, pressure
Wet Air Oxidation	COD, TOC, $S^=$, CN^-, specific organics	90+%	Offgases Sludge	Temperature, residence time, pressure, wastewater composition
Thermal Oxidation	TOC, red S/N, specific organics	99% (organics)	Flue gas Ash	Temperature, residence time, excess air, atomization
Gravity Separation	Tars/Oils TSS	60+% 10+%	Byproduct tars/oils Recovered solids/sludge	Temperature, residence time, relative density differences, particle size
Chemical Precipitation	Trace metals, dissolved solids	50+% (hardness)	Sludge	Reagent dosage, temperature, liquid composition
Dissolved Gas Stripping	NH_3, CO_2, H_2S, HCN, VOC	50+%	Stripped gases	Steam/feed ratio, number of stages, pH of feed liquor, reflux ratio, temperature, pressure
Filtration	TSS	30-80%[c] 80+%[d]	Spent filter media; backflush water	Filter media type, nature of solids, filtration rate, backwash frequency and effectiveness
Membrane Separation	TDS, TOC	N/A	Recovered condensate; wastewater concentrate	Membrane properties, nature of pollutants present, osmotic pressure
Forced Evaporation	TDS, TOC	N/A	Recovered condensate; wastewater concentrate, noncondensible gases	Recovery rate, demisting efficiency, condensate composition

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[a] Monitoring in the inlet stream to a control device could include the same substances/survey techniques considered for the outlet stream (Table 4-5). However, the emphasis fo· inlet stream monitoring might be placed on the major substances the device was designed to control. The "specific organics" mentioned in this column include the aliphatics, aromatics, oxygenates, nitrogenous compounds and/or sulfur containing compounds appropriate for each stream (see Table 4-5).

[b] Control device operating parameters to be monitored might be chosen from this column.

[c] Without pretreatment (flocculation/coagulation).

[d] With pretreatment (flocculation/coagulation).

TABLE 4-14. TYPICAL SYNFUELS PLANT CONTROL DEVICES AND KEY OPERATING VARIABLES--SOLID WASTE

Process	Substances Controlled[a]	Typical Controlled Efficiency	Secondary Discharge Streams	Major Control Device Operating Parameters Affecting Emission Levels
Landfill	All	N/A	Leachate Atmospheric emissions	Waste handling techniques Waste characteristics Site specific factors such as climate, topography, geology, hydrology
Incineration	Organics	>90%	Flue gas Residual ash	Waste characteristics Temperature Residence time Excess air
Stabilization	All	N/A	Leachate (at reduced levels) Atmospheric emissions	Type of process used Characteristics of wastes
Land Treatment	Organics	Unknown	Volatile organics as atmospheric emissions Leachate	Characteristics of wastes Site specific factors

[a] The solids/sludges entering these processes should be monitored according to the suggestions in Table 4-6. The "outlet" collected leachate from landfill should be monitored as suggested in Table 4-5 (generic stream Category 4). The flue gas and residual ash from incineration should be monitored as suggested in Table 4-4 (generic stream Category 2) and Table 4-6 (Generic Stream Category 4), respectively.

future control design decisions. However, in selecting substances to be monitored in the inlet stream, emphasis might be placed upon the main substances that the device was designed to control).

- The major control device operating parameters that affect discharge levels. (If the control device fails to operate as anticipated, the cause of the problem is likely to be reflected by one or more of these operating parameters.)
- Certain other information of possible interest in the design of the monitoring program (e.g., inlet pollutant loadings, secondary discharge streams).

The list of control devices in these tables does not necessarily include every control that might appear in a synfuels plant.. Nor are the lists of important operating parameters necessarily exhaustive. However, the tables should provide a basis for selecting monitoring that might be considered around control devices in most cases. Additional information on control devices is given in the PCTM references mentioned in Section 1.5.

4.2 A PHASED APPROACH FOR DATA BASE DEVELOPMENT

In Section 4.1, suggestions were provided regarding the possible extent of a data base for synthetic fuels plants. In Section 4.2, a specific phased monitoring approach is suggested by which a data base might be developed in a cost effective manner. In Section 4.3, additional, alternative monitoring approaches (some of which also envision some form of phasing) are described.

The total data base (e.g., as described in Tables 4-4 through 4-6) is reasonably extensive, and it will be costly to conduct this full monitoring program over an extended period. However, if the data base is to be useful in controlling the impacts of future synfuel plant replications, it is important that the data base be developed over an extended operating period. The data base would then reflect a range of plant cycles/operating conditions, and provide a sufficient data history for reliable extrapolation of the data base to other synfuel facilities. To satisfy the need for an extended monitoring period, while at the same time controlling monitoring costs, a phased approach is suggested.

If a two-phased approach is used, it would be reasonable for the first phase (Phase 1) to include:

- permit-mandated compliance monitoring,
- monitoring for the full ("baseline") data base for discharges (as defined in Tables 4-4 through 4-6) during routine plant operation (after shakedown), and
- monitoring of the performance of control technologies, as described in Section 4.1.3.

Phase 1 would continue only long enough to address practical considerations (e.g., to cover seasonal or other variations), and to provide a data base of sufficient accuracy and completeness for a specific facility. The results of the Phase 1 monitoring would be evaluated to select a limited number of "indicator" substances or parameters, which are shown in the Phase 1 data to be suitable (perhaps even semi-quantitative) indicators of fluctuations in other data base substances/parameters. This limited number of indicators would then be monitored in Phase 2, to represent the total data base. Accordingly, the content of Phase 2 would include:

- continued permit-mandated compliance monitoring,
- tracking the total discharge data base through the monitoring of a limited number of indicator substances/parameters, and
- tracking control technology performance, through the monitoring of major pollutants in and out, and perhaps monitoring of indicators and/or key operating parameters.

If fluctuations in a Phase 2 indicator suggest that the substances represented by that indicator have deviated outside of some expected range (i.e., that the Phase 1 baseline might have shifted), then Phase 1 analyses for the substances represented by that indicator might be repeated. The baseline would then be updated. Even if the indicators do not suggest such a deviation during Phase 2, periodic repeats of the Phase 1 analyses are suggested throughout Phase 2 to assure that the baseline has not shifted without being reflected in the indicators.

This phased approach should be developed to provide the data base described in Section 4.1 in a cost-effective manner. It is suggested the statistical procedures be used as a basis for developing Phase 1 of this plan (as described in the following sections). The use of statistical techniques to analyze Phase 1 data and then develop the Phase 2 plan is also suggested; however, it must be recognized that the extent (data quality and quantity) of the actual Phase 1 data base collected (which cannot be defined before implementation):

- will limit the type of statistical analysis that can be performed, and
- may require a restructuring of the overall approach to Phase 2 monitoring, especially if indicator species cannot be selected for a large number of "significant" parameters.

Although Phase 1 monitoring would not begin until shakedown is completed, monitoring should be useful during the shakedown period to:

- validate and perfect monitoring procedures, as part of quality assurance,
- train personnel, and
- initiate compliance monitoring as required by permits.

The suggested bases for selecting the frequency, timing and duration of Phase 1 monitoring according to this approach are described in Section 4.2.1. These bases include consideration of statistical principles to aid in the selection. Startup monitoring is addressed in Section 4.2.1.3. Phase 2 monitoring is discussed in Section 4.2.2.

4.2.1 Phase 1 Monitoring

As discussed previously, the intent of Phase 1 is to develop the total data base described in Section 4.1. This data base would then (with periodic updating) serve as the baseline for a reduced monitoring effort during Phase 2.

This section contains a discussion of the possible bases for selecting:

- the timing of Phase 1--when it might start, under what conditions monitoring might be considered,
- the frequency and duration of Phase 1 monitoring, considering both practical and statistical concerns, and
- the pre-Phase 1 monitoring that might be conducted during the plant startup period.

4.2.1.1 Phase 1 Timing

The objective of the Phase 1 monitoring is to develop "baseline" levels for parameters of interest. Thus, most of the Phase 1 monitoring should be conducted during routine operation after shakedown. However, the end of the shakedown period and the beginning of routine operation may not be a well-defined point. It is likely that different sections of a plant will follow different schedules in progressing through the shakedown process. The comments made in this section appear to assume that all Phase 1 measurements will be made at the same time. In practice, however, startup and lineout activities in a large, complex facility such as a new synthetic fuels plant are not likely to be simultaneous. This could be either intentional or the result of problems in sections of the plant. In either case, to be consistent with the objectives of the overall monitoring program, Phase 1 monitoring (in a given plant section) can be started as soon as the plant (or plant section) is lined out at design (or anticipated "normal") operating conditions.

In general, Phase 1 sampling should be performed when the plant is operating routinely within design parameters. Usually, data would not be collected during transient operations. However, a limited amount of information might be gathered during selected periods of scheduled transient performance to evaluate the effect of the transient on the baseline.

Even if plant operating variations prevent sample collection at exactly the planned frequency, the sampling should be performed at a fairly uniform rate (e.g., if six samples are desired over a one-year period, the samples should be collected at approximately bi-monthly intervals, rather than all samples being collected in a one-month period).

4.2.1.2 Frequency and Duration of Phase 1 Monitoring

The monitoring frequency should be selected for the various substances/parameters in the various streams based upon two major considerations:

- the availability of monitoring techniques--including their capabilities, turnaround time and costs, and
- the quality desired in the Phase 1 measurement data base for a specific site.

When the variability of a given substance or parameter is known (i.e., the standard deviation of analyses of a given stream in a given facility over a specific period of time), one can use statistical principles to estimate the number of measurements required to provide a desired accuracy for the mean estimate of that substance/parameter. The greater the variation in a parameter, and the greater the desired accuracy, the greater will be the necessary number of measurements. This number of measurements determines the relationship between the monitoring frequency and the duration over which monitoring is conducted. Because monitoring frequency and duration are linked in this manner, they are discussed together in this section.

The Phase 1 monitoring duration is also influenced by two major considerations:

- the desired accuracy, as discussed above
- practical considerations, including the desire to include within Phase 1 a reasonable range of plant operating conditions, and the desire to complete Phase 1 within some reasonable time period.

Thus, a number of factors must be weighed in order to decide upon a reasonable Phase 1 frequency and duration.

In Tables 4-15 through 4-17, a range of Phase 1 monitoring frequencies is suggested for the analyses and specific components listed in Tables 4-4 through 4-6. The availability of monitoring techniques and the significance of the stream categories were considered in defining the frequency ranges. Also considered was the need to keep monitoring costs to reasonable levels while obtaining a sample set which will provide data of reasonable accuracy. A rationale for the suggested frequency ranges is presented for each generic stream category listed in Tables 4-15 through 4-17. In addition, some criteria are given as a basis for choosing the appropriate frequencies.

TABLE 4-15. SUGGESTED PHASE 1 MONITORING FREQUENCY - GASEOUS DISCHARGE STREAMS

Generic Stream Category	Monitoring Frequency Suggestions		Comments
	Test Results of Interest	Possible Frequency Ranges[a]	
1. Boiler/Furnace flue gases from the combustion of conventional fuels	Criteria Pollutants	Q-C	Rationale: Continuous monitors are available for some criteria pollutants such as SO_2, NO_x, and particulates. In some cases, continuous monitoring may be less costly than periodic sample collection and analysis. Frequent monitoring may also be required by permit conditions. Quarterly monitoring represents the lowest frequency bound, because four samples in a one-year period are felt to be the minimum statistically desirable number. Considerations: Continuous monitoring for some criteria pollutants may be desirable as an aid in controlling combustion and/or operating pollution controls. The presence and levels of criteria pollutants in flue gases from combustion of conventional fuels have been studied in some detail. The combustion of natural gas and/or clean plant fuel gas is not expected to require very frequent monitoring - quarterly monitoring should be sufficient. More frequent monitoring of flue gases from the combustion of heavy liquid fuels (such as residual oils) may be desirable. The levels of some pollutants in the flue gases are generally related to process parameters such as feed stream properties, excess air rate, combustion temperature and furnace residence time. If adequate correlations can be developed, process parameter monitoring may reduce the need for more frequent pollutant monitoring.
2. Boiler/furnace, or incinerator flue gases from the combustion of process-derived fuels or waste streams	Criteria Pollutants	Q-C	Rationale: Continuous monitoring instruments are available for some criteria pollutants. In some cases, continuous monitoring may be simpler and less expensive than periodic sampling collection and analyses. Continuous or frequent monitoring of criteria pollutants may be required by permit conditions. Analyses of trace elements, sulfur/nitrogen species, and complex organics are somewhat more difficult, time consuming, and expensive. For that reason, monthly monitoring for these materials is the suggested upper frequency bound. Quarterly monitoring represents the lowest frequency bound, because four samples over a one-year period are felt to be the minimum statistically desirable number. Considerations: Continuous monitoring of criteria pollutants may be required by permits. If not required, lower frequency of monitoring might be acceptable. Continuous monitoring will provide more data than periodic sampling/analyses. More frequent monitoring of species, particularly heavy organics is important if heavy fuels (such as sludges, tars, and heavy waste gases) are being burned. Frequent sampling provides greater accuracy and better definition of baseline values. Sources in which synthetic fuel gases are being burned are less likely to have heavy organics present in flue gases. Monitoring of these streams for organics could be less frequent. It may be desirable to monitor flue gases more frequently during initial stages of monitoring. Frequency could be reduced later if the results of monitoring indicate a justification for less monitoring. The levels of some pollutants in the flue gases are generally related to process parameters such as feed stream properties, excess air rate, combustion temperature and furnace residence time. If adequate correlations can be developed, process parameter monitoring may reduce the need.
	NMHC	Q-M	
	Reduced Sulfur and Nitrogen Species	Q-M	
	Volatile Trace Elements	Q-M	
	Trace Elements	Q-M	
	Aliphatic and Aromatic Organics	Q-M	
	TCO/GRAV	Q-M	
	Nitrogenous Organic Compounds	Q-M	
	Organics in Table 4-8	Q-M	

(Continued)

TABLE 4-15. (continued)

Generic Stream Category	Monitoring Frequency Suggestions: Test Results of Interest	Monitoring Frequency Suggestions: Possible Frequency Ranges[a]	Comments
3. Uncombusted vent gases or feed gases to flare	Criteria Pollutants	Q-C	**Rationale:** Continuous monitoring instruments are available for some criteria pollutants, and continuous or frequent monitoring of these compounds may be required by permit conditions. In some cases, continuous monitoring may be simpler and less expensive than periodic sample collection and analyses. Analyses of trace elements, sulfur/nitrogen species, and complex organics are somewhat more difficult, time consuming, and expensive. Thus, monthly monitoring for these materials is the suggested upper frequency bound. Quarterly monitoring represents the lowest frequency bound, because four samples over a one-year period are felt to be the minimum statistically desirable number. **Considerations:** Continuous monitoring of criteria pollutants from some of the vent gas streams may be required by permit. If not required, lower frequency of criteria pollutant monitoring might be acceptable. Continuous monitoring will provide more data than periodic sampling/analyses. More frequent sampling is indicated for those streams which can be expected to vary as a result of varying feed composition, feed rates, or discharge rates. It is virtually impossible to measure flare emissions at the source. The feed to the flare is generally highly variable, so monthly monitoring should be considered. Compounds of particular interest in the flare feed are sulfur/nitrogen compounds, volatile trace elements, and refractory organic compounds which are less easily combusted. It may be desirable to monitor some of the vent streams more frequently during the early stages of the monitoring effort. The frequency could be reduced later in the program for those streams which contain consistent and/or low levels of pollutants.
	NMHC	Q-M	
	Reduced Sulfur and Nitrogen Species	Q-M	
	Volatile Trace Elements	Q-M	
	Trace Elements	Q-M	
	Aliphatic, Aromatic and Oxygenated Organics	Q-M	
	TCO/GRAV	Q-M	
	Nitrogenous and Sulfur Containing Organic Compounds	Q-M	
	Organics in Table 4-8	Q-M	
4. Tank Vents	Reduced Sulfur and Nitrogen species	SA-BM	**Rationale:** Tanks can be present in relatively large numbers in synfuels plants. Thus, frequent sampling of these sources can be expensive and time consuming. Tanks are generally dedicated to particular liquid services, and the composition of the vented gases will only change significantly with the tank temperature and the composition of the contents. The composition of the tank vent gases can be expected to change somewhat over the year as the ambient temperature changes. Bimonthly sampling should be sufficient to detect significant composition differences (if they exist) throughout the year. If composition changes are not significant, or if the hydrocarbon content of the vapor is low, the monitoring frequency could be reduced as low as twice a year. **Considerations:** Fixed-roof tanks generally are used to store hydrocarbon liquids of relatively low volatility. Obviously, the most volatile of these liquids can be expected to produce vented gases with the highest concentrations of hydrocarbons. Examples of relatively volatile liquids which might be stored in fixed-roof tanks are unstabilized or unhydrotreated products and by-products. The composition of the vapor above the liquid at any given temperature and pressure is a function of the liquid composition. The results of early monitoring efforts could be used to define the accuracy and consistency of these relationships between liquid and vapor compositions. If the relationships are valid, liquid samples could be periodically analyzed to confirm that no significant changes in the concentration of components of interest have occurred. Vapor analyses could thus be significantly reduced or even replaced by liquid analyses.
	Total Hydrocarbons	SA-BM	
	Volatile Aliphatics, Aromatics and Oxygenates	SA-BM	
	NMHC	SA-BM	
	Organics in Table 4-8	SA-BM	

(Continued)

TABLE 4-15. (continued)

Generic Stream Category	Monitoring Frequency Suggestions: Test Results of Interest	Monitoring Frequency Suggestions: Possible Frequency Ranges[a]	Comments
5. Process Fugitive Emissions	Total VOC Concentration	SA-Q	Rationale: Process fugitive emissions can be controlled through a periodic leak detection and repair (LDAR) program. The cost of this type of program can be quite significant, although for some sources (such as valves), the cost can be partially or completely offset by the value of the recovered material. The major cost item is the monitoring or detection segment of the program, and this cost rises exponentially as the frequency of monitoring increases. The program becomes particularly costly at monitoring intervals of less than three months (quarterly). Results of a LDAR program may well show that the leak frequency and/or leak occurrence rate for some sources is quite low. In these cases, the monitoring frequency may be reduced as low as twice a year. Considerations: Sources in service on streams consisting of light (volatile) hydrocarbons and gases are most prone to emit fugitive emissions. Streams containing less than 10 percent of combined hydrocarbon, CO, H_2S, and NH_3 can generally be exempted from monitoring. Careful records of the results of the monitoring program should be kept. Such records may indicate particular streams or sources which have very low leak frequencies and leak occurrence rates. Petroleum refinery and chemical plant studies have shown that processes in which heavy liquids are dominant have low rates of fugitive emissions. Examples are vacuum distillation, lube oil processing, and asphalt production. Monitoring results in these types of units can be expected to justify semi-annual monitoring frequencies. More frequent monitoring of streams containing toxic and/or noxious components (such as H_2S and NH_3) may be desirable to keep fugitive emissions of these compounds at a low level.
	Carbon Monoxide	SA-Q	
	H_2S	SA-Q	
	NH_3	SA-Q	
	Volatile Aliphatics and Aromatic Compounds	SA-BM	
6. Fugitive emissions from waste impoundments, storage and disposal facilities	VOC	SA-BM	Rationale: Fugitive emissions from these sources can be expected to be highly variable due to the variability of the material sent to the sources, as well as changes in weather conditions (for exposed sources, in particular). Direct measurement of emissions from these sources is generally impractical and very costly (if it can be done at all). Thus, monitoring will probably consist of ambient air monitoring (upwind/downwind) in the immediate vicinity of the individual sources. Ambient-air monitoring is costly and time consuming. It is also subject to a considerable degree of uncertainty, so a reasonable number of samples are necessary to adequately define the emissions. Bi-monthly sampling represents a compromise between the cost of sampling and the need for accuracy. Initial monitoring may show only small degrees of variation with time, and the monitoring frequency could be reduced to as low as twice a year. Semi-annual sampling is felt to be the lower bound of monitoring frequency to obtain samples in at least two different seasons of the year (such as hot/cold, wet/dry). Considerations: Experience in petroleum refineries and chemical plants has indicated that sources with large exposed areas in which organic material is directly exposed to the air (uncovered oil-water separators, dissolved air flotation units, land treatment sites) may emit significant quantities of VOC and other volatile compounds. Aerated sources such as aeration ponds, biological oxidation units, aerated activated sludge units, and dissolved-air flotation units can also be expected to emit detectable quantities of VOC and other volatile compounds. More frequent monitoring (particularly in the early stages of the monitoring program) should be considered for these sources. In some cases, the VOC content of the water, sludge, etc. being processed in these sources can be determined. This may also guide the selection of initial monitoring frequencies. The absence of significant amounts of VOC in the water and/or waste material may justify a lower monitoring frequency.
	H_2S	SA-BM	
	Particulates	SA-BM	

(Continued)

TABLE 4-15. (continued)

Generic Stream Category	Monitoring Frequency Suggestions		Comments
	Test Results of Interest	Possible Frequency Ranges[a]	
7. Fugitive Particulate Emissions	Particulates	SA-BM	**Rationale**: Particulate emissions are a function of the source properties, level at which the source is being worked/disturbed, and weather conditions. Since particulate sampling is relatively costly, bimonthly monitoring was selected as a compromise between the need for accuracy and the monitoring cost. The results of initial testing may justify reduction of that frequency as low as semi-annually because of either consistency of emissions or low emissions levels. **Considerations**: Fugitive particulate emissions can be expected to be very erratic around active sources such as coal storage piles, coke production and storage, and raw material (such as oil shale) transportation. Areas in which the wind is relatively strong and/or variable should produce varying particulate emission levels. Such sources should be monitored with greater frequencies to define the emissions as accurately as practical. Those sources such as reserve coal storage, and wet coal/coke/shale piles can be expected to emit particulates at a low rate, and even initial monitoring of such sites may be done at frequencies less than bimonthly.

[a] A = annual, SA = semiannual. Q = quarterly, BM = bimonthly, M = monthly, BW = bi-weekly, W = weekly, C = continuous

NOTE: Flow rates and temperatures of discharge streams should be monitored at the same frequency as the chemical composition. Likewise, major pertinent process variables should be monitored at this same frequency (e.g., feedstock feed rate to plant, feedstock composition).

TABLE 4-16. SUGGESTED PHASE 1 MONITORING FREQUENCY-AQUEOUS DISCHARGE STREAMS

Generic Stream Category	Monitoring Frequency Suggestions: Test Results of Interest	Monitoring Frequency Suggestions: Possible Frequency Ranges[a]	Comments
1. Wastewaters discharged to outfalls, impoundments, or deep wells that are not unique to synfuels plants and have their origins in organic-laden environment	Water quality parameters	SA-BM	Rationale: These wastewaters are not unique and are expected to be relatively benign in nature. In the absence of more stringent permit (NPDES) requirements, bimonthly monitoring during Phase 1 should be sufficient to include most operating conditions which are subject to seasonal variations. Initial results may justify a reduction in sampling frequency to a level as low as two times per year. Statistical and practical considerations suggest semiannual sampling as the minimum useful sampling frequency.
	Aliphatic and aromatic organic compounds	SA-BM	
	Trace elements	SA-BM	
2. Wastewaters discharged to outfalls, impoundments, or deep wells that are not unique to synfuels plants, and have their origins in an essentially organic-free environment	Water quality parameters	SA-BM	Considerations: NPDES permit requirements may dictate the monitoring frequency for these streams. In selecting a monitoring frequency for a given stream, the time constraints (or residence times) of various surge vessels/ponds should be considered. Another consideration is the known or anticipated nature of the stream. Since these streams are not unique to synfuels processing, some indication of their quality can be obtained from examining the nature of similar streams in other industries (such as the petroleum refining, petrochemical, and organic chemical industries). Initial monitoring frequencies as low as quarterly may be justified. However, test results should be carefully analyzed, and the presence of any unexpected compounds may indicate a need for additional or more frequent monitoring to verify water quality and organics content. If any of the stream parameters are to be considered as an indicator, the more frequent monitoring schedule is advisable.
	Trace elements	SA-BM	

(Continued)

TABLE 4-16. (continued)

Generic Stream Category	Monitoring Frequency Suggestions		Comments
	Test Results of Interest	Possible Frequency Ranges^a	
3. Wastewaters discharged to outfalls, impoundments, or deep wells that result from the quenching, cooling, purifying, upgrading, etc. of the plant's main products	Water quality	O-W	Rationale: Because of the generally unknown nature of these wastewaters and the uncertainty of wastewater treatment technologies in synfuels service, more frequent monitoring is suggested, particularly in the early stages of the plant operation. The cost of these tests must be weighed against the benefits achieved with larger sample populations. The highest monitoring frequencies suggested here represent a compromise between cost and data needs. The water quality parameter analyses are rather costly, but such testing is often an integral part of the wastewater treatment system operation. Weekly monitoring is suggested in the early stages of the plant operation, since both the water quality and the effectiveness of treatment will likely be uncertain and/or fluctuating. Monthly monitoring for other compounds should provide data over the range of seasonal variations in processing, ambient conditions, and product specifications. Twelve data sets per year provide sufficient data to statistically evaluate the quality and content of the effluent water as well as the effectiveness of wastewater treatment processes. Continuous biological screening is a relatively cost-effective method for determining the overall ecological effect of the treated wastewater on marine life. Other health and ecological tests should be performed on a bimonthly to quarterly frequency during the initial stages of plant operation. Quarterly sampling provides enough data sets for statistical purposes, particularly if variability is not great. However, initial monitoring frequencies should be greater until the range and variability of some of the parameters have been defined, or at least estimated. Considerations: The quality of the effluent water is a function of the plant processes and their operation, as well as the performance of the wastewater treatment system. Both the processing and the treatment may be quite variable during the first phases of the plant operation, and the higher frequency monitoring should be emphasized during this period. Some monitoring frequencies may also be dictated by permit (such as NPDES) requirements. High temperature gasification processes produce wastewaters which contain relatively low concentrations of organic compounds. On the other hand, the wastewaters from liquefaction and low/medium temperature gasification processes can be expected to contain higher levels of organics. Thus, it is particularly important that the effluent wastewater from these latter processes be monitored for organic compounds on a frequent basis. Those parameters which are considered as potential indicator compounds/parameters should be monitored at the higher frequencies to provide correlations/relationships of the highest possible accuracy. Results of the testing should be analyzed on a regular basis to determine if and when the frequency of monitoring can be reduced. Statistical analyses of the data should provide considerable guidance in defining the variability of the results and an acceptable level of reduced monitoring (if such a reduction is justified at all).
	Trace elements	O-M	
	Aliphatic, aromatic, and oxygenated organic compounds	O-M	
	Nitrogenous organic compounds	O-M	
	Sulfur-containing organic compounds	O-M	
	Volatile trace elements	O-M	
	Biological screening	SA-C	
	Organics in Table 4-8	O-M	

(Continued)

TABLE 4-16. (continued)

Generic Stream Category	Monitoring Frequency Suggestions: Test Results of Interest	Monitoring Frequency Suggestions: Possible Frequency Ranges[a]	Comments
4. Wastewaters discharged to outfalls, impoundments, or deep wells that are unique to synfuels facilities, but not included in Category 3	Water quality parameters	Q-W	Rationale: Much of the rationale discussed under Category 3 is applicable here. Although the levels of organics are expected to be low, this is not a certainty, and reasonably frequent monitoring (monthly) should provide data for a practical statistical assessment of the water quality and the levels of the various compounds in the effluent wastewater. At the same time, this level of monitoring should not be excessively costly. In general, the higher frequency level is suggested for initial definition of the wastewater quality and its expected variability. The lower suggested frequencies may be applicable in later stages of plant operation. Quarterly monitoring is the recommended lower limit for the monitoring frequencies. This level of monitoring still provides enough information for statistical evaluation and reasonably accurate water quality estimates (provided that the variability is not too great). Considerations: NPDES (and possibly other) permit requirments may require specific monitoring frequencies. More frequent monitoring should be performed during the initial phases of plant operation, since the water quality and levels of pollutants/contaminants will probably be quite variable. The concentrations of organic compounds in these streams are expected to be very low. If initial testing verifies this expectation, the organic compound monitoring frequency could be decreased to four times per year at a relatively early date. It may be desirable to maintain higher monitoring frequencies for those parameters which are to serve as indicator compounds/parameters. The results of the testing and analyses should be periodically reviewed to define both the levels and the variability of the water quality parameters and pollutants of concern. Those parameters/pollutants which have low variabilities or which are present at very low levels may be monitored at lower frequencies. NPDES (and possibly other) permits may require specific monitoring tests and frequencies. Obviously, these requirements would take precedence over the tests/frequencies suggested here if the suggested monitoring is less stringent than required in the permit(s).
	Trace elements	Q-M	
	Aliphatic and aromatic organic compounds	Q-M	
	Volatile trace elements	Q-M	
	Biological screening	SA-C	
	Organics in Table 4-8	Q-M	

[a] A = annual, SA = semiannual, Q = quarterly, BM = bimonthly, M = monthly, BW = bi-weekly, W = weekly, C = continuous

NOTE: Flow rates of discharge streams (to outfalls, impoundments, or deep wells) should be monitored at the same frequency as the chemical composition. Likewise, major pertinent process variables should be monitored at this same frequency (e.g., feedstock feed rate to the plant, feedstock composition).

TABLE 4-17. SUGGESTED PHASE 1 MONITORING FREQUENCY - SOLID WASTE DISCHARGES

Generic Stream Category	Monitoring Frequency Suggestions		Comments
	Test Results of Interest	Possible Frequency Ranges[a]	
1. Organic-laden solid wastes not unique to synfuels plants	Trace elements (whole sample and leachate)	SA-BM	Rationale: These streams are expected to be relatively benign in nature. The primary purpose of the monitoring is to define the physical and chemical properties of the wastes and to identify potentially leachable constitutents. Bi-monthly monitoring during the initial phases of the plant operation should satisfy these needs. Six data sets in the first year of monitoring should provide the basis for a statistically sound estimate of the various parameters and properties. A high degree of accuracy is not required for these parameters. Semi-annual monitoring is suggested as a lower frequency limit. This provides the minimum number of annual samples which can be statistically evaluated. The lower frequency should only be initiated for those nonhazardous streams which have relatively constant and/or low values for the parameters of interest. Considerations: Two of the main objectives of the monitoring are to satisfy regulatory (RCRA) requirements/constraints and to confirm that these wastes are not unique to synfuels facilities. Since these streams are not unique, some initial estimates of their composition may be developed from an examination of similar streams in other similar industries (i.e., petroleum refinery, petrochemical, and chemical industries). If initial monitoring confirms these levels, it may be possible to justify reduced frequencies for monitoring at a relatively early period of plant operation.
	Leachable aliphatic and aromatic organic compounds	SA-BM	
	TCO/GRAV	SA-BM	
	Ultimate and proximate analyses	SA-BM	
	RCRA hazardous waste tests	SA-BM	
	Particle size	SA-BM	
	Radioactivity	SA-BM	
2. Organic-free or organic-lean solid wastes not unique to synfuels plants	Trace elements (whole sample and leachate)	SA-BM	All of the monitoring tests suggested for Category 1 and 2 streams may not be practical or appropriate for all of the individual streams within the generic categories. The various monitoring tests required for the individual streams will have to be selected on an individual basis.
	Ultimate and proximate analysis	SA-BM	
	RCRA hazardous waste tests	SA-BM	
	Particle size	SA-BM	
	Radioactivity	SA-BM	

(Continued)

TABLE 4-17. (continued)

Generic Stream Category	Monitoring Frequency Suggestions		Comments
	Test Results of Interest	Possible Frequency Ranges^a	
3. Organic-laden solid wastes unique to synfuels plants	Trace elements (whole sample and leachate)	Q-M	**Rationale:** Solid waste streams in this category will be significant discharge sources and should receive major emphasis in a solid discharge characterization program. The suggested upper monitoring frequency of monthly sampling/analysis is a compromise between the need for characterization data and the high cost of frequent monitoring. Monthly monitoring will provide twelve data sets in a year. This data base should be sufficient to provide statistically valid estimates of the various parameters at a reasonable cost. At later stages of plant operation, after many of the solid waste characteristics have been reasonably well defined, the monitoring frequencies may be reduced. Quarterly monitoring is suggested as a lower limit. Four samples per year still provide enough data to allow statistical evaluations. Monitoring at frequencies less than four times a year is not suggested because of the potential importance of these discharges and the need to maintain a continual awareness of any changes that may occur in the wastes. **Considerations:** Some of the streams in this generic category may only be available intermittently (spent catalysts, for example), and these streams should be sampled as they are available to obtain the desired number of samples. It may not be practical to perform all the desired tests on every waste discharge in this category. The monitoring tests required for each specific stream will have to be selected on an individual basis. High temperature gasification processes will tend to produce discharge streams containing relatively low concentrations of organic compounds. Conversely, discharge streams from liquefaction and low/medium temperature gasification processes can be expected to contain higher levels of organic components. It is particularly important, therefore, that the solid waste streams from these latter processes be monitored for organic compounds on a frequent basis. The data from the sampling and analysis program should be examined frequently to identify those streams for which the monitoring frequencies can be reduced. Some streams may contain very low levels of some of the compounds under investigation. In other cases, some of the compounds and/or parameters may be found to be quite consistent during plant operation. In these cases, reduced frequency of monitoring can be justified after early stages of plant operation. Those parameters which are potential indicator compounds/parameters should be monitored at the higher frequencies to develop correlations and other relationships having the greatest possible accuracy.
	Extractable aliphatic, aromatic, and oxygenated organic compounds	Q-M	
	TCO/GRAV	Q-M	
	Extractable nitrogenous and sulfur-containing organic compounds	Q-M	
	Ultimate and proximate analysis	Q-M	
	RCRA hazardous waste tests	Q-M	
	Particle size	Q-M	
	Radioactivity	Q-M	
	Selected water quality parameters for leachates	Q-M	

(Continued)

TABLE 4-17. (continued)

Generic Stream Category	Monitoring Frequency Suggestions: Test Results of Interest	Monitoring Frequency Suggestions: Possible Frequency Ranges[a]	Comments
4. Organic-free or organic-lean solid wastes unique to synfuels plants	Trace elements	Q-M	**Rationale:** Much of the discussion of rationale presented for the Category 3 streams (see above) is also applicable here. The levels of organic compounds in the Category 4 solid waste discharge streams are expected to be quite low. Since this assumption is not a certainty, however, reasonably frequent (monthly) monitoring is suggested during the initial phases of plant operation. Monitoring at these frequencies should provide data for a practical statistical assessment of the levels of organic compounds present in the solid waste discharge streams. At the same time, the monitoring costs should not be excessive. The higher monitoring frequencies are suggested during the early phases of plant operation to provide an initial characterization of solid waste discharge stream properties and the variabilities of these properties. The suggested lower frequencies may find application during later plant operations. Quarterly monitoring is suggested as a lower limit for the monitoring frequencies. This level of monitoring can still develop enough information for statistical evaluations with reasonably accurate estimates of the solid waste parameters/properties (provided that the variability is not too great). **Considerations:** The more frequent monitoring is most applicable during the first phases of plant operation. This monitoring will allow reasonably accurate definition of baseline values for many of the solid waste stream parameters of concern. At the same time, the more frequent monitoring will provide some assessment of the variability of the solid waste properties. The concentrations of organic species in these solid wastes are expected to be low, by definition. In particular, those streams associated with high temperature coal conversion should be particularly low in or free of organic compounds. If initial monitoring verifies the expected low organic levels, the monitoring of organic compounds could be decreased to a frequency as low as four times per year at a relatively early stage of plant operation. It may be desirable, however, to maintain the higher frequencies for those parameters which are potential indicator parameters/compounds.
	Extractable aliphatic and aromatic organic compounds	Q-M	
	Ultimate and proximate analyses	Q-M	
	RCRA hazardous waste tests	Q-M	
	Particle size	Q-M	
	Radioactivity	Q-M	
	Selected water quality parameters for leachates	Q-M	

[a] A = annual, SA = semiannual, Q = quarterly, BM = bimonthly, M = monthly, BW = bi-weekly, W = weekly, C = continuous

Tables 4-15 through 4-17 address monitoring frequencies for discharge streams only. Where monitoring is being conducted around environmental control devices, it is expected that monitoring of the control inlet and key operating parameters (as discussed in Section 4.1.3) will be conducted at the same time as monitoring of the control discharge.

The number of measurements required in Phase 1 is a function of two major factors:

- the variability of the parameters being measured (as reflected, for example, by the standard deviation of the parameter). There are several contributing components to variability: variability of both the environmental sampling procedures and the analytical effort; and both short-term and long-term variability in the synfuels process itself;
- the desired quality of the data base from Phase 1 measurements. The data base quality can be selected to fit the needs of a specific parameter at a specific site and, as such, can be controlled by the program designer.

Since the selection of the quality level of the Phase 1 data base can play a major role in determining the number of measurements, this selection is an important responsibility of the program designers. The quality of the Phase 1 data base impacts not only the confidence in the baseline data base, but also the accuracy and the approach with which the baseline can be tracked during Phase 2 (see Section 4.2.2.2). The intent of the following paragraphs is to provide background that will aid the user in selecting the desired data base quality for a parameter. An expanded discussion of the concepts described in this section is included in Appendix B.

The quality of the data base for a specific parameter is concerned with how well actual measured values reflect variations in actual discharge parameters or emission levels over the time period represented by the data base. A set of measured values is usually summarized in terms of the central tendency (mean) and the dispersion (standard deviation) for the parameter. The mean and standard deviation can be used in conjunction with an appropriate distribution model to represent expected parameter levels.

Confidence intervals (see Appendix B) can be used to evaluate the expected precision of estimates of the mean for a parameter using the Phase 1 data base. A confidence interval for the mean is a set of end points about the average obtained from sample measurements that is believed, with a specified degree of confidence, to include the parameter mean. The parameter mean is defined here as the value which would be obtained if continuous measurements were made and averaged for the period. The confidence level for a confidence interval indicates the expected percentage of the time that a constructed interval will actually include the parameter mean. For a particular distribution model, the width of the confidence interval for the mean depends on:

- the variability of the measurement (standard deviation or coefficient of variation),
- the confidence level (90%, 95%, 99%, etc.), and
- the sample size (number of measurements made during Phase 1).

The relationship between data variability and the number of samples required to establish a given level of precision for the parameter mean at the 95 percent confidence level is given in Table 4-18. This table shows the effects of variability and number of samples or data points on the expected confidence interval around a calculated mean. The variability is expressed in terms of a known coefficient of variation. This coefficient is defined as the ratio of the known standard deviation and the known mean, and it is expressed as a percent.

An example of how to use Table 4-18 follows. This example is for a parameter having a coefficient of variation of 50 percent for which the normal distribution is an appropriate model. If six measurements were made (n=6) the 95 percent confidence interval (from Table 4-18) has an expected range of ±52 percent of the mean of the six measurements. That is, the expected confidence interval ranges from 0.48 times and 1.52 times the mean of the six measurements.

TABLE 4-18. EXPECTED CONFIDENCE INTERVALS FOR A PARAMETER MEAN AS A FUNCTION OF NUMBER OF SAMPLES (MEASUREMENTS)

Expected Variability of Measurement (Coefficient of Variation)[a]	Distribution (Model)	95% Confidence Interval About the Mean Estimate for Phase 1 (percent)[b]					
		n = 4 (Quarterly)[c]	n = 6 (Bi-monthly)[c]	n = 12 (Monthly)[c]	n = 24 (Semi-monthly)[c]	n = 52 (Weekly)[c]	n = 365 (Daily)[c]
5%	Normal Model	±8.0	±5.2	±3.2	±2.1	±1.4	±0.5
	Lognormal Model	+8.1,-7.5	+5.4,-5.1	+3.2,-3.0	+2.1,-2.0	±1.4	±0.5
10%	Normal Model	±15	±11	±6.4	±4.2	±2.8	±1.0
	Lognormal Model	±17,-15	+11,-9.9	+6.5,-6.1	+4.3,-4.1	+2.8,-2.7	±1.0
25%	Normal Model	±40	±26	±16	±11	±6.9	±2.6
	Lognormal Model	+48,-32	+29,-23	+17,-14	+11,-9.9	+7.1,-6.6	+2.6,-2.5
50%	Normal Model	±80	±52	±32	±21	±14	±5.2
	Lognormal Model	+110,-53	+62,-39	+35,-26	+22,-18	+14,-12	+5.0,-4.8
100%	Normal Model	±160	±110	±64	±42	±28	±11
	Lognormal Model	+280,-73	+104,-58	+70,-41	+42,-30	+26,-21	+9.0,-8.2
200%	Lognormal Model	+650,-87	+280,-74	+124,-55	+71,-42	+43,-30	+14,-12
500%	Lognormal Model	+1700,-94	+570,-85	+220,-68	+120,-53	+65,-40	+20,-17
1000%	Lognormal Model	+3000,-96	+900,-90	+300,-75	+150,-60	+82,-45	+24,-20
10000%	Lognormal Model	+13000,-99	+2300,-96	+590,-85	+260,-72	+130,-57	+37,-27

[a] Coefficient of variation is the ratio of the standard deviation to the mean expressed in percent.
A known value for the coefficient is assumed in this table.
If the coefficient of variation is greater than 100%, the normal model is not realistic.

[b] n = number of samples or data points.

[c] Monitoring frequencies required for the specific value of n if the duration of Phase 1 was one year.

Confidence intervals are shown in Table 4-18 for both normal and lognormal distribution models (Appendix B). Most populations of discharge stream measurements can be represented reasonably well by one of these cases. Discharge stream parameters which tend to have low values and be limited on the "bottom end" by zero, but which can assume occasional high values as well (e.g., fugitive emission leak rates), frequently follow a log normal distribution. Other parameters will not be limited to some minimum value and will more often follow a normal distribution pattern.

The confidence intervals given in Table 4-18 can be used to evaluate alternative Phase 1 testing frequency and duration decisions. The product of the frequency and the Phase 1 duration will determine the sample size available for estimating the mean. Table 4-18 contains confidence interval widths expressed as a percent of the mean. Sample sizes range from n = 4 to n = 365. Variabilities range from a coefficient of variation (CV) of 5 percent to a CV of 10,000 percent.

To further illustrate the use of Table 4-18, consider a variable that varies symmetrically about its mean value (normal distribution) with an assumed coefficient of variation of 50 percent. The fourth row in Table 4-18 describes data with a CV of 50 percent. Reading across the fourth row, one can see that the width of the confidence interval decreases as more samples are taken. If 6 samples are taken, the 95 percent confidence interval is ±52 percent. With 365 samples, the interval is reduced to ±5.2 percent. Table 4-19 summarizes this example. Tables such as this can be used to evaluate trade-offs between the cost of testing and the precision of the estimated mean (both of which increase as the sample size increases).

As another example of using Table 4-18, suppose it is important to estimate the parameter mean within a confidence interval of about 50 percent. Table 4-18 can be used to determine the number of samples required to maintain this confidence interval (with a confidence level of 95 percent) for parameters with different variabilities (CVs). The results shown below are applicable for either a normal or log-normal model.

CV of Parameter	Number of Samples Required (n)	Required Test Frequency For Phase 1 Duration of One Year
<25%	4	quarterly
25 - 50%	6-12	bi-monthly
50 - 100%	24	semi-monthly
100 - 500%	52	weekly
>500%	365	daily

The calculations reflected in Table 4-18 can be repeated for other sets of conditions (e.g., for other confidence levels, CV's, or sample sizes). The equations used for making these calculations are presented in Appendix B. It is generally felt that a 95% confidence level is reasonable for this type of analysis.

Table 4-18 focuses on how well a parameter mean can be estimated (i.e., the confidence interval about the mean). Confidence intervals can also be calculated for the standard deviation to evaluate how well the variability of a parameter can be estimated from the data base. A statistician should be contacted for this type of analysis.

TABLE 4-19. PRECISION OF THE ESTIMATED MEAN AT A 95 PERCENT CONFIDENCE LEVEL FOR VARIOUS SAMPLE NUMBERS (CV = 50%; NORMAL DISTRIBUTION MODEL)

Number of Samples	Frequency for a One Year Duration[a]	Precision of Estimated Mean
6	bi-monthly	±52%
12	monthly	±32%
24	semi-monthly	±21%
52	weekly	±14%
365	daily	±5%

[a] monitoring frequency required to obtain the indicated number of samples if Phase 1 duration is one year

The coefficient of variation for the various parameters in synfuels plant discharges is likely to vary from parameter to parameter. It is expected that the coefficient of variation for many synfuels parameters will be reasonably high (over 30%).

The manner in which the monitoring program designer might utilize these statistical concepts in selecting Phase 1 frequency and duration is suggested schematically in Figure 4-2. The steps in this procedure include:

- estimate (order of magnitude) the coefficient of variation for the various parameters. Since the coefficient will likely be different for every parameter, the designer might wish to assume one or more gross values for the coefficient and categorize the parameters of interest according to which gross value most reasonably might apply.
- select the desired accuracy for estimating the parameter mean during Phase 1. This step would involve selection of the desired confidence level (e.g., 95%) and confidence interval (e.g., ±50%). This selection of Phase 1 accuracy could influence (or be influenced by) the desired accuracy and approach for tracking the parameters during Phase 2, as discussed in Section 4.2.2.2.
- select the reasonable number of measurements (from Table 4-18 or equivalent), considering the estimated coefficients of variation and the desired accuracy. As a practical matter, this selection will likely be a judgment made by the designer after reviewing the sample number versus confidence interval tradeoff reflected in Table 4-18.
- select the frequency and duration, based upon the selected sample number. Here again, the program designer will need to make judgments concerning the frequency-versus-duration tradeoff, based upon the particular circumstances. The availability/costs of monitoring techniques, and the desire for the Phase 1 duration to encompass a reasonable period of time, will undoubtedly influence these judgments.
- conduct the Phase 1 monitoring, and interpret the results (including calculation of the parameter mean, coefficient of variation, and confidence interval).

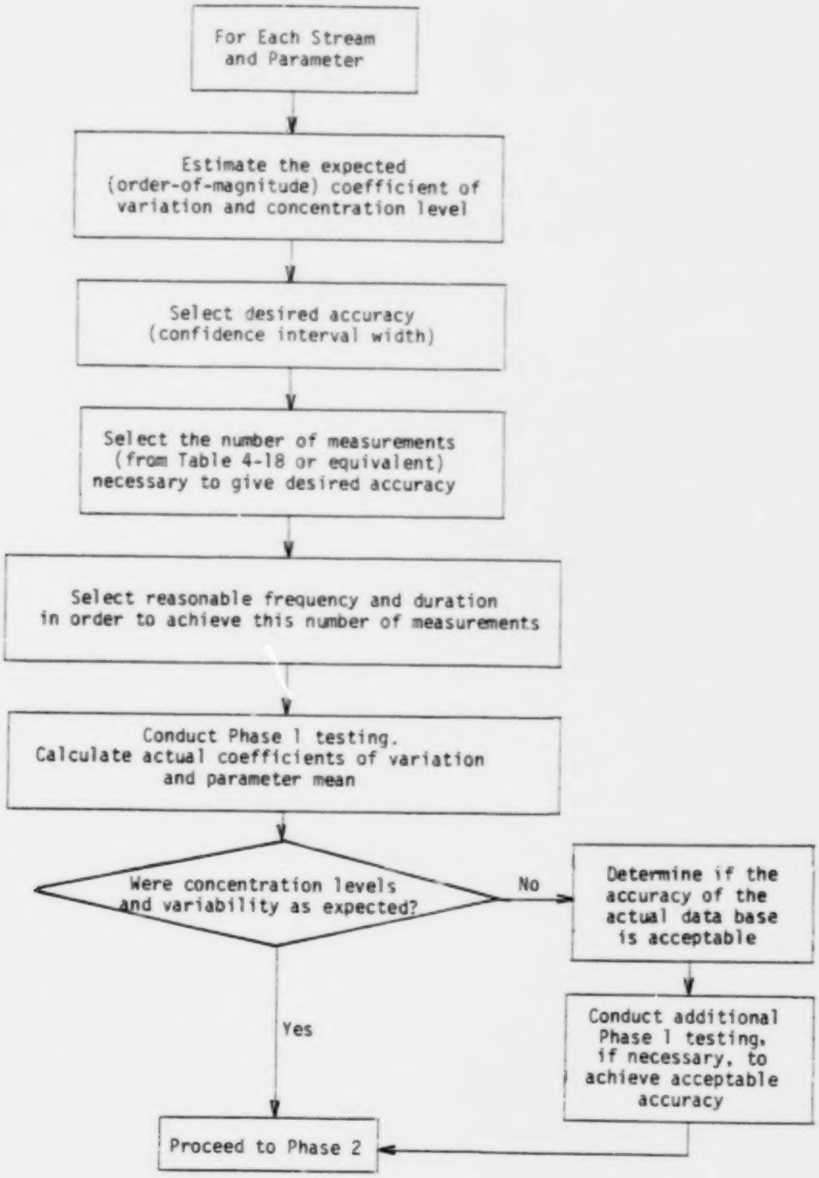
For Each Stream and Parameter
Estimate the expected (order-of-magnitude) coefficient of variation and concentration level
Select desired accuracy (confidence interval width)
Select the number of measurements (from Table 4-18 or equivalent) necessary to give desired accuracy
Select reasonable frequency and duration in order to achieve this number of measurements
Conduct Phase 1 testing. Calculate actual coefficients of variation and parameter mean
Were concentration levels and variability as expected?
No
Determine if the accuracy of the actual data base is acceptable
Conduct additional Phase 1 testing, if necessary, to achieve acceptable accuracy
Yes
Proceed to Phase 2

Figure 4-2. Schematic diagram of approach for selecting Phase 1 monitoring frequency and duration.

- if the observed parameter levels are substantially different than expected, the impact of this discrepancy should be assessed. If the coefficient of variation is actually much higher than was anticipated, and if the attained confidence interval is thus much broader than had been desired, it might be decided that a larger number of Phase 1 measurements is needed to achieve the desired confidence interval. In this case, Phase 1 testing for that parameter might be continued for an additional period.

Sample numbers, monitoring frequencies and durations derived using the above approach would be tailored to each site, and would provide Phase 1 results of known quality. While the decisions for any one site will vary depending upon the site, some typical considerations are discussed below:

- Sample number. Although calculations such as Table 4-18 might suggest a certain number of measurements as being adequate (e.g., n=6 for SO_2), it might be more convenient (or required by permit) that a greater number of samples be taken in some cases (e.g., continuous monitoring for SO_2). Conversely, for more difficult measurements (e.g., GC/MS for complex organics), it might be reasonable to limit sample number to, e.g., 4 to 12, in order to keep cost and duration reasonable, even if this number results in an accuracy somewhat lower than desired. As indicated earlier, Phase 1 sample number can also be influenced by the method selected for interpreting Phase 2 data.

- Duration. A reasonable duration would have to be selected for each site based upon statistical considerations, as discussed above, and based upon practical considerations, such as the desire to cover a reasonable range of plant operating conditions, and the desire to limit Phase 1 to a reasonable length. While the selection of duration is site specific, a duration of approximately one year might be reasonable in many cases. This duration would cover any seasonal variations and many other long-term process variations, and could provide time for a reasonable number of sampling events.

- Frequency. The frequency ranges shown in Tables 4-15 through 4-17 reflect both practical considerations (e.g., the capabilities, turnaround times and costs of monitoring techniques) and the intuitive significance of the stream categories involved. The selection of a monitoring frequency from within these ranges would be based upon the circumstances of each specific synfuels facility, including the statistical considerations described previously. In some cases, it might be desirable to select a frequency outside of the range indicated on the table (e.g., if a substance of particluar concern has a high coefficient of variation, or if a permit specifies a particular frequency outside the range).

Stability of the Phase 1 Baseline

The discussion in this section assumes that the concentration levels for a particular parameter and stream during Phase 1 can be represented by a single baseline distribution. The variation observed in parameter concentrations during Phase 1 is assumed to be due to random causes (i.e., sampling and analytical variability and random process variability). A single mean and coefficient of variation (or standard deviation) can thus be used to characterize the Phase 1 baseline data.

If in fact, a synfuels plant operates at systematically different conditions during Phase 1, more than one baseline may be appropriate. For example, two different types of coal might be used for the feedstock (e.g., low-sulfur and high-sulfur coal). Certain parameter discharge levels may be systematically affected by the change in coal type. The parameter concentrations would thus form two different distributions depending on the types of coals used during the monitoring period. These distributions would have different means and possibly different variations. The statistical considerations discussed in this section would then be applicable to each distribution. For the affected parameters, separate baselines for each condition should be evaluated against the incremental costs of developing multiple data bases.

There may be other important changes in operating conditions during Phase 1, in addition to coal type, that could also affect measured parameter values. During the interpretation of the Phase 1 results, statistical procedures can be used to evaluate stability, if adequate measurements are available. For example, if twelve or more data points are available, a control chart (reference 4-32) can be constructed to evaluate the stability of the process. The control chart will identify segments of the data which should be described by different baselines. When a large amount of data is available (e.g., from daily testing or continuous monitors) more sophisticated techniques, such as time series analysis (reference 4-33) or response surface analysis can be used to evaluate the effects of changes in plant operating conditions or parameter levels. A statistician should be consulted for these analyses.

As discussed later, shifts in the baseline can have beneficial impacts in some cases. Data obtained at more than one baseline can aid in the statistical selection of indicators to represent the data base during Phase 2 monitoring (see Section 4.2.2.1).

4.2.1.3 Monitoring During the Plant Startup Period

The intent of Phase 1 monitoring is to develop a representative, "baseline" data base for the synfuels facility. Thus, a comprehensive Phase 1 testing program would not normally be proposed during the startup period, because the facility would be expected to be operating at non-representative, transient conditions during this period. However, some monitoring would be of value during startup to:

- validate and refine monitoring procedures, as part of the QA/QC program (discussed in Section 3.0),
- train personnel,
- conduct permit-required compliance monitoring.

The data collected during the startup monitoring may not contribute directly to the "baseline" data base. However, the startup monitoring results should be reviewed as a possible aid in the design/conduct of Phase 1. These results can also serve as an indication of possible startup discharges from future replications of the synfuels technology.

Validation and refinement of the monitoring procedures are necessary for several reasons. The exact characteristics of many synfuel plant discharge streams cannot be established until some operating experience with the specific process is obtained. As a result, some of the monitoring procedures that the program designer might expect to apply, might have to be adjusted or changed to be more compatible with the substances which are present. For example, the nature of the organics actually present could influence the analyst's selection of an extraction method; or the presence of interfering compounds could influence the selection of an appropriate detector. Other validation procedures are described in Section 3.0.

To accomplish this validation/refinement, it is suggested that two separate monitoring campaigns be conducted during the plant startup period. Each campaign would consist of a full Phase 1 effort (as defined by the survey techniques and specific component analyses identified in Tables 4-4 through 4-6). These campaigns should involve a review of the performance of the techniques and monitoring personnel, and a review of the results, in order to assess whether any of the techniques should be modified.

For a complete QA/QC program, these two startup monitoring campaigns might also include elements aimed at determining sampling and analytical variability. A discussion of these elements is presented in Section 3.0.

The first of the two startup monitoring campaigns would logically be initiated as soon as possible after plant startup, and the second conducted within 3 to 6 months after the first. The sampling might be conducted during "reasonable" plant operating conditions, but the plant will likely be operating at transient or part-load conditions during the startup period.

If startup of a section of the plant extends beyond 3 to 6 months, it might be desirable to continue monitoring for major substances in key streams during startup of that section after the two campaigns discussed above are completed. This continuing startup monitoring might logically include only the specific substances listed in the column, "Specific Component Suggestions", in Tables 4-4 through 4-6. Continued analysis for trace metals or complex organics identified through the survey techniques might not be warranted during the transient startup period, unless the surveys during the two startup campaigns suggest consistently high levels of some substance of particular concern.

During the startup, limited monitoring might also be conducted around some of the major control devices. This would be aimed at assuring that the controls are operating basically as anticipated. The monitoring would not be intended to characterize control performance during the non-representative startup period. The testing would logically address only the major pollutants that the control device was designed to remove, as distinguished from the entire list of survey techniques/specific components listed in Tables 4-4 through 4-6. Such pre-Phase 1 control monitoring would help assure that the controls will be operating properly when routine operation begins after startup, and that routine operation will not be delayed by inadequate control performance. It might be expected that this type of control performance checking during startup would normally be conducted by the plant operator in any event.

4.2.2 Phase 2 Monitoring

During the Phase 1 monitoring effort, a comprehensive, "baseline" data base will be developed. The intent of Phase 2, in the approach being described here, is to monitor this total data base without having to monitor for every parameter contained in the data base. The method suggested to accomplish this goal is the use of a limited number of "indicator parameters" to represent everything in the data base. These indicators will be selected, to the extent possible, from the relationships observed in the Phase 1 data between the indicators and the parameters they represent. In theory, if the selected indicator remains at its observed Phase 1 level throughout Phase 2, then the represented parameters can also be assumed to remain at their Phase 1 level. If, during Phase 2, the indicator varies from its Phase 1 level, a single Phase 1 monitoring program might be conducted for the stream in which the excursion occurred and for the substances represented by the indicator that varied. The baseline data base would thus be continually updated, based upon the Phase 2 results for the indicator parameters and the Phase 1 repeats for the varying parameters.

Due to the inherent uncertainties in selecting indicators and in measuring the indicators during Phase 2, it is possible that the baseline might shift without being reflected by an excursion of the indicators outside of the accepted limits. To guard against such an undetected baseline shift, Phase 1 testing might be repeated periodically during Phase 2, even if not triggered by an indicator excursion.

This section contains a discussion of:

- methods for selecting indicator parameters and steps that might be taken if effective indicator relationships are not apparent,
- criteria for deciding when a Phase 2 indicator result suggests that the baseline has shifted,
- frequency of Phase 2 monitoring needed to detect important baseline shifts with reasonable confidence, and,
- periodic repeats of Phase 1 to assure that an undetected baseline shift has not occurred.

4.2.2.1 Selection of Indicator Parameters for Phase 2

A key element in the phased approach is the selection of a limited number of indicators which can effectively represent the total Phase 1 data base. The relationship between the indicator and the species it represents should be developed from review of the Phase 1 data.

Indicators might include: individual chemical compounds; some measure of a class of compounds; gross chemical parameters, such as COD or TOC; plant or control device operating conditions; perhaps even bioassays. Conceivably, an indicator could provide an index for several classes of species. By definition, the indicator would have to be monitored during Phase 1.

The selection of candidate indicators can be based on:

- observed statistical relationships between the indicator and the substances it represents as developed from the Phase 1 data, or
- theoretical correlations from engineering analysis or fundamental chemistry.

If a theoretical correlation is employed, it would be desirable to test the relationship as additional data become available from Phase 2.

Statistical principles can be used to determine indicator relationships. As will be discussed, the nature of the relationship between an indicator and the parameters it represents can vary. In a few cases, a true quantitative relationship might be apparent; i.e., if the indicator changes in concentration by a certain amount, then the represented parameter changes by a certain corresponding and predictable different amount. More often, the relationship will be "semi-quantitative"; i.e., if, during Phase 2, the indicator remains within its range observed during Phase 1, then the represented parameters also might be expected to remain within their Phase 1 ranges. In some cases, a parameter might show _no_ correlation with any other potential indicator (i.e., it would have to be its own indicator for a time).

The procedure for selecting indicators basically consists of two steps: 1) identification of which observed Phase 1 parameters might be considered, from a practical point of view, to be suitable potential indicators; and 2) exploring alternative statistical correlations to see if relationships might be identified between the observed parameters and the potential indicators.

Identification of Potential Indicators

Table 4-20 is intended to aid in the identification of potential indicators. The types of potential indicators are presented in Table 4-20 and are discussed below in order of increasing specificity.

TABLE 4-20. TYPES OF POTENTIAL INDICATORS FOR PHASE 2 MONITORING

Indicator	Basis of Relationship	Class or Category of Compounds Potentially Indicated
o OPERATING PARAMETERS		
- Main Reactor Feedstock composition: ultimate, proximate, trace elements Steam/O_2 ratio Reactor temperature and pressure Reactant and product flowrates	Changes in feedstock composition, operating conditions and flowrates may result in changes in emission levels; for example; if feed volatile carbon increases, organic loading may increase; or if product flowrate decreases, trace element emissions may decrease.	Organics and inorganics
- Raw Reactor Effluent Cooling Recycle, blowdown, makeup rates Differential pressures Operating temperatures and pressures		
- Gas Purification and Upgrading Flowrates Operating temperatures and pressures Differential pressure Recycle, blowdown, makeup rates Regeneration steam rates		
- Liquid Product Separation and Upgrading Flowrate of aqueous and hydrocarbon phases Operating temperatures and pressures		
- Products Synthesis Reactant and product flowrates Operating temperatures and pressures		
- Control Technologies See Tables 4-12, 4-13, and 4-14 for operating parameters affecting emission levels		
o NON-SPECIFIC CHEMICAL ANALYSES		
Total Organic Carbon (TOC)	Provides indication of change in total aqueous organic loading	Organics and some water quality parameters
Total Inorganic Carbon (TIC)	Provides indication of change in total aqueous inorganic carbon loading	Carbonate, bicarbonate, and some water quality parameters
Chemical Oxygen Demand (COD)	Provides indication of change in total aqueous organic loading	Organics and some water quality parameters
Total Chromatographable Organics (TCO)	Provides indication of change in total extractable organic loading	Organics
Gravimetric Organic Loading (GRAV)	Provides indication of change in total extractable organic loading	Organics
Total Hydrocarbon Analysis	Provides indication of change in total vapor phase organic loading	Organics

(Continued)

TABLE 4-20. (continued)

Indicator	Basis or Relationship	Class or Category of Compounds Potentially Indicated
Methane/Nonmethane Hydrocarbon Analysis by FID	Provides indication of change in total vapor phase organic loading	Organics
Infrared Analysis (IR)	Provides indication of change in organic class distribution or composition	Aliphatics, aromatics, oxygenates (ethers, esters, ketones, carboxylic acids)
GC-Photoionization Detection	Provides indication of change in aromatic organic distribution or composition	Simple aromatics
Ultraviolet Analysis	Provides indication of change in polynuclear aromatic organic distribution or composition	Polynuclear aromatics
Fluorescence Spot Test	Provides indication of change in polynuclear aromatic organic distribution or composition	Polynuclear aromatics
GC-Nitrogen Specific Detection	Provides indication of change in nitrogenous organic distribution or composition	Nitrogenous compounds
Colorimetry (4-aminoantipyrine)	Provides indication of change in distribution or composition of phenolics	Phenolics
GC-Sulfur Specific Detection	Provides indication of change in distribution or composition of sulfur containing compounds	Sulfur containing compounds
o SPECIFIC COMPONENTS		
- Permit Required Monitoring Will vary with specific permit requirements. Could include, for example, CO	Might provide indication of change in emission composition or distribution. For example, a change in flue gas CO levels could indicate a change in combustion efficiency that would also affect organic emissions	Specific permit monitoring requirements might provide indications for organics and/or inorganics
- Non-Regulated Components	May serve as indicator of change in concentration of members of a class of analogous compounds	
Hexane		Aliphatics
Benzene		Simple Aromatics
Napthalene		Polynuclear Aromatics
Aniline and Carbazole		Amines and heterocyclic nitrogen compounds
Acetonitrile		Nitriles/isocyanates
Phenol		Phenolics
Acetic Acid		Carboxylic acids
2-Hexanone and Dibenzofuran		Other oxygenates
Benzothiophenes		Sulfur containing compounds

Operating conditions are the simplest type of parameter which may serve as indicators of change in stream compositions and emission levels. For example, incinerator temperature changes may indicate changes in the organics in the off-gas. The operating parameters listed in Table 4-20 may prove to be suitable potential indicators for organic and/or inorganic components.

Non-specific chemical analyses may serve as indicators for certain categories of compounds. For example, a change in TOC may indicate a change in specific organics in a wastewater stream. Several potential indicators of this type are shown in Table 4-20.

Specific components may also serve as indicators for classes of compounds or homologous series of compounds. Some of these specific components may be monitored as a result of permit requirements or they may be non-regulated. Examples of these specific components and the classes of compounds they may indicate are also shown in Table 4-20. An advantage to utilizing less specific indicators is that they often are less expensive or time consuming to implement than the more specific indicator analyses.

Since many organic compounds may potentially be present in some streams, the indicator compounds given in Table 4-20 may not be sufficient to represent complex mixtures. Therefore, Table 4-21 presents additional potential indicator compounds which may be explored as potential indicators for the organic substances of interest in synfuels waste streams listed in Table 4-10. Further details for the use of non-specific chemical analyses as indicators are also given in Table 4-21. Table 4-21 follows the same organic compound classification as Table 4-10. Alternative potential indicator compounds and non-specific chemical analysis indicators (where applicable) are shown for each organic classification. To provide additional information for the user, some specific examples of compounds previously identified in synfuels waste streams are included under the appropriate categories in this table. Often,

TABLE 4-21. CANDIDATE INDICATORS FOR ORGANICS OF INTEREST IN SYNFUELS WASTE STREAMS

Category of Organics[a]	Compound Name	Indicators Non-Specific Chemical Analysis[b]	 Specific Compounds
(Subcategory)	General (Specific Example Compounds)		
ALIPHATICS	Alkanes (Pentane) (Hexane) (Heptane) (Octane)	Infrared Analysis[b] at characteristic wavelength	Hexane Eicosane
	Cycloalkanes (Cyclohexane) (Methyl Cyclohexane)		
	Alkenes		
	Alkadienes (Butadiene) (Cyclohexene)		
AROMATICS (Single-ring)	(Benzene [BP 80°C]) Alkyl Benzenes (Ethyl Benzene [BP 136°C]) (Methyl Styrene) (Toluene) (Xylene [BP 137-144°C])	GC/PID[b] (Retention time window corresponding to organics with boiling points 65°C to 200°C)	Benzene[b]
(Multi-ring, non-fused)	Biphenyls (Biphenyl [BP 245-255°C]) (Dimethylbiphenyl) (Methylbiphenyl)	GC/PID[b] (Retention time window corresponding to organics with boiling points 200°C to 300°C)	Biphenyl
(Multi-ring, fused)	Indanes/Indenes (Indan [BP 176°C]) (1H Indene)	GC/PID[b] (retention time window corresponding to organics with boiling points 100°C to 350°C, melting point 300°C	Indan

(Continued)

TABLE 4-21. (continued)

Category of Organics[a]	Compound Name	Indicators	
		Non-Specific Chemical Analysis[b]	Specific Compounds
POLYNUCLEAR AROMATICS	Naphthalenes		
	(Methylnaphthalene)	Fluorescent Spot Test[b]	Naphthalene[b]
	(Dimethylnaphthalene)		
	(Ethylenenaphthalene)		
	(Naphthalene [BP 218°C])		
	(Trimethylnaphthalene)		
	(Tetramethylnaphthalene)		
	(Phenylnaphthalene [PB 324-325°C])		Phenylnaphthalene
	Anthracenes/Penanthrenes		Anthracene/Phenanthrene
	(Anthracene [BP 312°C])		
	(Phenanthrene [BP 336°C])		
	(Chrysene [BP 448°C])		
	(4H-Cyclopenda(def)phenanthrene)		
	(Dimethylphenanthrene/Dimethylanthracene)		
	(Dimethylpyrene)		
	(Methylanthracene/Methylphenanthrene)		
	(Methylbenz(a)anthracene)		
	(Methylchrysene)		
	(Methylcyclopenta(def)phenanthrene)		
	(Methylpyrene)		
	(Pyrene [BP 393°C])		
	(Trimethylanthracene)		
	(Trimethlphenanthrene/Trimethylanthracene)		Pyrene
	Acenaphthenes		
	(Acenaphthene [BP 279°C])		Acenaphthene
	(Acenaphthylene [BP 280°C])		
	(Methylacenaphthene)		
	(Dimethylancenaphthene)		
	(Bimethylacenaphthene)		
	Benz(a)anthracenes		
	(Benz(a)anthracene [MP 160°C])		
	(Benz(a)anthracene/Chrysene)		
	(7,12-Dimethylbenz(a)anthracene)		
	Benzo Pyrenes		
	(Benzo(a)pyrene [MP 179°C])		Benzopyrene
	(Methylbenzo(a)pyrene)		

(Continued)

TABLE 4-21. (continued)

Category of Organics[a]	Compound Name	Indicators Non-Specific Chemical Analysis[b]	Indicators Specific Compounds
POLYNUCLEAR AROMATICS (Continued)			
	Dibenz Anthracenes (Dibenz(a,h)anthracene [MP 226°C])		
	Perylenes (Perylene [sub 350/450°C]) (Benzo(g,h,i)perylene) (Dibenzoperylene)		Perylene
	Fluorenes (Benzofluorene [MP 209-102°C]) (11H Benzo(a)fluorene) (Dimethylfluorene) (Fluorene [BP 298°C]) (Methylfluorene)		
	Fluoranthenes (Fluoranthene [BP 394°C]) (Methylfluoranthene) (Dimethylfluoranthene)		Fluoranthene
	Benzofluoranthenes (Benzo(k)fluoranthene)		
	Indenopyrenes		
	Cholanthrenes (Methylcholanthrene [MP 179-180°C])		Methylcholanthrene
NITROGENOUS COMPOUNDS Amines and Heterocycles (Amines)	Anilines (Aniline [BP 184-186°C])	GC/N specific[b] (retention time window corresponding to organics with boiling points 50°C to 400°C)	Aniline[b]
	Alkyl Anilines/Diamines		
	Naphthylamines (2-Naphthylamine [BP 306°C])		2-Naphthylamine
	Aromatic Amines		
	Aminobiphenyls		
	Morpholines (Morpholine [BP 129°C)		

(Continued)

TABLE 4-21. (continued)

Category of Organics[a]	Compound Name	Indicators: Non-Specific Chemical Analysis[b]	Indicators: Specific Compounds
NITROGENOUS COMPOUNDS (Continued)			
(Heterocyclic Nitrogen Compounds)	Pyridines (Pyridine [BP 115-116°C])	GC-N specific[b] (retention time window corresponding to organics with boiling points 50°C to 400°C)	Pyridine[b]
	Carbazoles (Carbazole [BP 335°C]) (Methylcarbazole)		Carbazole[b]
	Quinolines (Quinoline [BP 238°C])		
	Acridines (Acridine [BP >346°C])		
	Pyrroles (Pyrrole [BP 130-131°C])		
	Indoles (Indole [BP 253°C])		
OXYGENATES (Phenolics)	Phenols (Phenol [MP 35-40°C])	Colorimetry(4-aminoantipyrene)[b]	Phenol[b]
	Alkyl Phenols (Dimethyl Phenol) (Methyl Phenol) (Tetramethylphenol) (Trimethyl Phenol)		
	Naphthols (2-Naphthol [122-123°C]) (Methyl Naphthol)		Naphthol
	Dihydric Phenols (Resorcinol [MP 109-110°C])		
	Benzofuranols		

(Continued)

TABLE 4-21. (continued)

Category of Organics[a]	Compound Name	Indicators Non-Specific Chemical Analysis[b]	 Specific Compounds
OXYGENATES (Continued)			
Carboxylic Acids	Alkyl Acids (Formic Acid [116-118°C]) (Acetic Acid [100.8°C])	Infrared Analysis[b] at characteristic wavelength	Acetic Acid[b]
	Aromatic Acids (Benzoic Acid [122-123°C])		Benzoic Acid
Other Oxygenates (Ethers)	Alkyl Ethers	Infrared Analysis[b] at characteristic wavelength	
	Aromatic Ethers		
	Dioxanes		
(Alcohols)	Alkyl Alcohols (Butanol)	Infrared Analysis[b] at characteristic wavelength	Butanol
	Cycloalcohols		Cellosolve
	Cellosolves (2-Ethoxyethanol [BP 135°C])		
(Ketones)	Alkyl Ketones (2-Butanone) (2-Heptanone [BP 149-150°C]) (3-Heptanone [BP 146°C]) (2-Hexanone [BP 127°C]) (4-Methyl-2-pentanone [BP 117-118°C]) (5-Methyl-3-heptanone) (2,6-Dimethyl-4-heptanone [169°C]) (2-Pentanone) (2-Propane)	Infrared Analysis[b] at characteristic wavelength	4-Methyl-2-pentanone
	Cycloketones		
	Aromatic Ketones		
(Aldehydes)	Formaldehyde	Infrared Analysis[b] at characteristic wavelength	
	Alkyl Aldehydes		
	Aromatic Aldehydes		Benzaldehyde
(Esters)	Alkyl Esters	Infrared Analysis[b] at characteristic wavelength	
	Aromatic Esters (Phthalate Esters)*		

(Continued)

TABLE 4-21. (continued)

Category of Organics[a]	Compound Name	Indicators	
		Non-Specific Chemical Analysis[b]	Specific Compounds
OXYGENATES (Continued)			
(Heterocyclic Oxygen)	Furans (Furan [BP 32°C])	None available (possibly GC/PID)	Furan
	Benzofurans (Methylbenzofuran [BP 197°C])		
	Dibenzofurans (Dibenzofuran [BP 285°C]) (Dimethyldibenzofuran) (Methyldibenzofuran)		Dibenzofuran
SULFUR CONTAINING (Mercaptans and Sulfides)	Alkyl Mercaptans (Methyl Mercaptan [BP 6°C]) (Ethyl Mercaptan) (Butyl Mercaptan [BP 64-98°C])	GC-S specific[b] (retention time window corresponding to organics with boiling points 5°C to 150°C)	Ethyl Mercaptan
	Alkyl Disulfides (Methyldisulfide [BP 110°C])		
(Heterocyclic Sulfur)	Thiophenes (Thiophene [BP 84°C])	GC-S specific[b] (retention time window corresponding to organics with boiling points 75°C to MP 200°C)	Thiophene
	Benzothiophenes (Benzo(b)thiophene [BP 221°C]) (Benzo(b)naphtho(1,3-d)thiophene) [MP 186°C])		Benzothiophene[b]

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[a] As listed in Table 4-10.

[b] Given in Table 4-20.

*Generally present as artifacts of sample handling and exposure to plastics. Not anticipated to be produced in synthetic fuels processes.

non-specific chemical analysis results will be adequate to confirm any compositional changes or indicate the absence of a class of organic compounds; and more rigorous and quantitative analyses for specific indicator compounds will not be necessary.

No specific inorganic indicator compounds have been suggested for the elements listed in Table 4-11. Since the elements listed in Table 4-11 will most often be identified not as compounds but as total elemental concentration, the element will most commonly serve as an indicator for itself. Most of the elements listed in Table 4-11 can be identified rapidly in an ICP analysis of each sample; therefore, no selection of indicator elements for classes of elements (analogous to Table 4-21) has been made. Analysis of some volatile elements, arsenic, antimony, selenium and mercury, by AA is still most commonly applicable; and it will probably be necessary to quantify each of these elements individually by AA. Once elements of interest have been selected from the Phase 1 data, the details of implementation for the analytical techniques (e.g., ICP) may change in Phase 2 to focus on these specific elements. If indicators beyond those suggested in Table 4-20 are desired for the elements listed in Table 4-11, the selection of those indicators should be based on an analysis of both the process design and process chemistry.

When Tables 4-20 and 4-21 are used for a specific Phase 1 data set, the program designer would review the Phase 1 data base to identify the classes of organics and to determine if potential indicator compounds have been observed. The program designer then might employ the statistical data interpretation techniques, discussed later, to determine if the Phase 1 data set reflects suitable relationships between the potential indicators and the compounds or groups of compounds the indicators were to represent. An assessment would be made to determine if operating parameters might be used as indicators. Then, the program designer might determine if non-specific chemical analyses may be appropriate as Phase 2 indicators. Tables 4-20 and 4-21 then would be applied to select potential indicators. For compounds observed in a specific Phase 1 data set but not listed in Table 4-21, judgments would be necessary to categorize the observed compounds. Selection of potential indicator compounds would be made using Table 4-21 as a guide. If no indicators can be identified, then rigorous definition of indicators will be delayed until further data become available.

The selected indicators should have some practical, as well as statistical, relationship to the parameters being represented. For example, the indicator might be a member of a homologous series of organic compounds representing other compounds in that series; it might be a gross organic parameter (non-specific chemical analysis), such as TOC representing specific organics in a wastewater stream; or it might be an operating parameter, such as incinerator temperature representing organic compounds in the off-gas.

Exploring Alternative Correlations between Potential Indicators and Represented Parameters

A variety of statistical procedures are available for quantifying indicator/parameter relationships from monitoring data. (These procedures are discussed later.) The appropriate statistical procedure will depend on the form of the available data and the expected indicator relationship.

Some Potential Difficulties in Developing Indicator Relationships. The development of suitable relationships between potential indicators and Phase 1 parameters that they might represent during Phase 2 might be complicated by two factors:

- the relatively small amount of data which may be available from Phase 1, especially for those parameters for which monitoring is expensive and time consuming.
- the variability of the sampling and analysis procedures relative to the range in concentration of the parameters during the Phase 1 period. To evaluate potential indicator relationships, the range of the parameter concentrations during the Phase 1 period should be much larger than the analytical variability. Since Phase 1 tests might be at a single set of "baseline" operating conditions for the plant (i.e., at a stable baseline), some parameter values might not vary significantly

during Phase 1. Thus, it is possible that data obtained from Phase 1 might not be adequate to develop quantitative indicator relationships for some parameters.

The nature of this problem is illustrated in Figure 4-3, where measured values for a hypothetical parameter of interest are plotted against a potential indicator for that parameter. A series of measurements at "normal", or baseline, plant operating conditions are indicated in the figure by the letter N. As shown, any correlation that might exist between the parameter and the potential indicator is hidden by the effects of sampling and analytical variability. However, in this hypothetical example, if plant operation were changed to a different set of conditions (a new baseline), representing an "excursion" from the original baseline (represented by the letter E in the figure), the effect of this change might be large enough to override the effects of sampling and analytical variability. Then the nature of the overall relationship might be revealed. The initial Phase 1 monitoring will be limited in duration, and might be deliberately aimed at a single set of "baseline" conditions. It is possible that the range of plant operating conditions during Phase 1 might not be great enough to effectively reveal some relationships which might in fact exist. The potentially limited number of samples obtained during Phase 1 would only exacerbate this problem.

To validate indicator/parameter relationships, it would be desirable to collect data over a wide range of operating conditions. The parameters of interest should vary as widely as possible for the purpose of defining any indicator relationships. If a synfuels plant is being operated at a different set of conditions as part of the plant operating plan, then Phase 1 monitoring (of potential indicators and represented parameters) could profitably be scheduled to occur during operations at these different conditions. Such Phase 1 monitoring might be conducted during the initial Phase 1 period, if the baseline shift occurs then, or it could be one of the Phase 1 repeats scheduled during Phase 2 (discussed later).

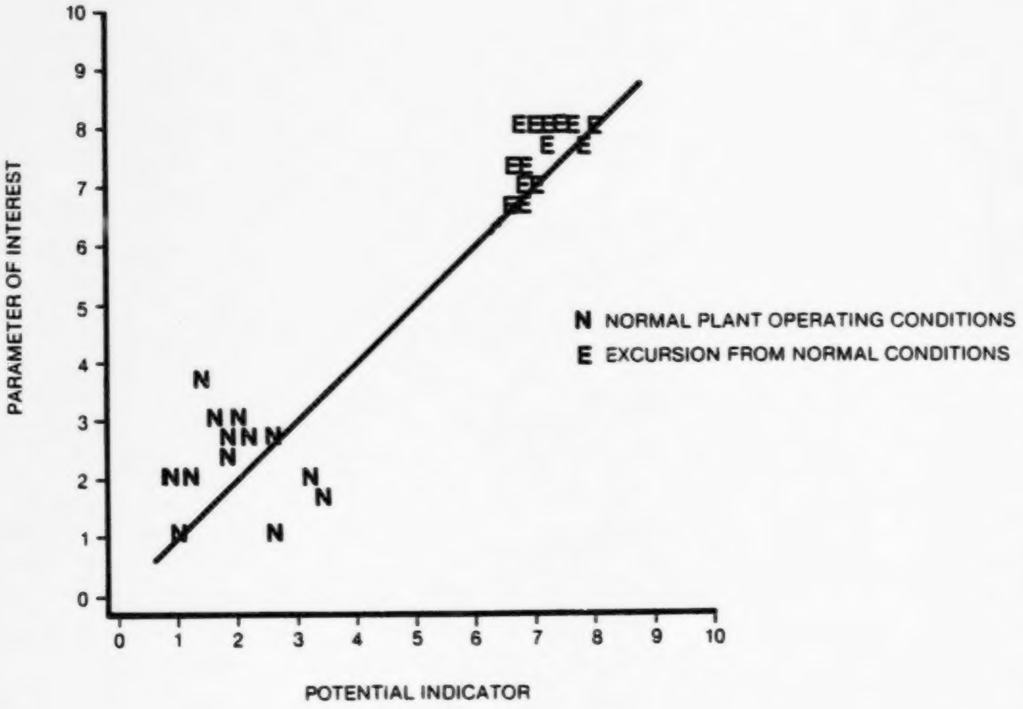

Figure 4-3. Determining indicator/parameter relationships.

Development of Indicator Correlations when Data Permits. If available data include adequate variations for both the parameters and potential indicators, statistical procedures can be used to evaluate and quantify the form of the relationship between a parameter to be represented and its potential indicator. Various statistical techniques might be applied to the Phase 1 data in exploring potential qualitative and quantitative relationships between the alternative candidate indicators and the parameters to be represented. Some of these more useful techniques are summarized in Table 4-22.

When quantitative data sets are available, techniques such as correlation analysis, regression analysis and several of the multivariate procedures are most applicable in analyzing the potential indicator/parameter relationships. Multivariate techniques are also useful for screening multiple candidate indicators. The strength of an indicator/parameter relationship can be defined using correlation analysis. Regression analysis is useful in developing quantitative relationships (if present) between indicators and the represented parameters.

Many of the parameters of interest in synfuels plants will be present at levels which logically fall into discrete ranges of values. A good example of this type of behavior is the presence of compounds of interest in concentrations at or below analytical detection limits. Discriminate analysis and categorical data analysis procedures are useful when dealing with this type of data.

Approach when Data do not Permit Statistical Indicator Correlations. If indicators cannot be identified from the Phase 1 data/results, alternative approaches can be developed for proceeding with Phase 2 testing. For example, indicator/parameter relationships can be developed based on fundamental chemistry considerations or derived from an engineering analysis of the plant/process operation. Alternately, Phase 2 could proceed and "temporary" indicators could be used. As discussed later, the complete Phase 1 testing should

TABLE 4-22. STATISTICAL TECHNIQUES AND THEIR APPLICABILITY TO THE ANALYSIS OF MONITORING PROGRAM DATA

Technique	Applicability	Result of Application	Limitations	References
1. Correlation Analysis	1. To indicate the degree to which variations in one parameter are "tracked" by corresponding variations in another parameter (e.g., a candidate indicator). This is probably one of the most familiar, easily applied and useful tests of the strength of an indicator/monitored parameter relationship.	1. A correlation coefficient, r, is calculated by the method described in Appendix B. r^2 is then used as a measure of the degree to which two variables "track" one another. $r^2 > 0.9$ indicates a strong correlation (good indicator/parameter relationship). $r^2 < 0.1$ indicates a poor correlation. Utility of values between 0.1 and 0.9 would depend upon situation.	1. Data for both the parameter and the indicator must be quantitative (i.e., not simply detected/not detected or low-medium-high). Since this technique assumes a linear relationship, initial cross-plots may be needed to determine the best possible correlation form. Data transformations (e.g., to log domain) may be useful in establishing the strongest possible correlations.	4-34
2. Regression Analysis (Method of least squares)	2. To develop a quantitative expression for the relationship between a monitored parameter and its indicator(s). This technique will provide a more definitive indication of indicator/parameter relationships than that provided with correlation analysis.	2. An equation which can be used to predict the value of a parameter of interest given a set of assumed or measured indicator parameter values.	2. The existence of a statistically significant indicator/parameter relationship which can be quantified through an equation, may imply more of a cause-effect relationship than is appropriate; see also limitations 1 and 3.	4-34
3. Discriminant analysis	3. To develop a relationship between a potential indicator and substances it might represent, when the represented substances fall into discrete classes (e.g., detected vs. not detected) and where the potential indicator is quantified (numerical values available).	3. A relationship which describes the probability of a parameter falling into some class or range of values given a known set of quantitative values for appropriate indicators.	3. A lot of analysis can be required to develop appropriate correlation forms, select appropriate class ranges, etc.; see also limitation 2.	4-35

(Continued)

TABLE 4-22. (continued)

Technique	Applicability	Result of Application	Limitations	References
4. Categorical Data Analysis (Chi-square test)	4. To develop a relationship between a potential indicator and substances it might represent, when the represented substances fall into discrete classes (e.g., not detected, detected, quantified) and where the indicator parameter itself is expressed as an element of a discrete class of values. (e.g., low, medium, or high).	4. A definition of whether a statistically significant relationship exists and a definition of error rates for specific indicator/parameter relationships.	4. Similar to limitations for technique 3.	4-36
5. Other Multivariate Procedures (e.g., canonical correlation, principal component analysis, factor analysis, cluster analysis)	5. To analyze relationships among multiple parameters and indicators simultaneously. Can be valuable in screening alternative indicator/parameter relationships and in selecting the best single indicator or group of indicators for larger classes or groups of monitored parameters.	5. Depends on technique; allows quick screening of alternatives; indicator indexes can be developed.	5. Requires a large data base compared to some of the other techniques to establish meaningful correlations.	4-35

be periodically repeated throughout Phase 2 in order to determine whether the baseline has shifted without excursions in the indicators. To aid in indicator selection, these Phase 1 test programs could be scheduled when the plant is operating (at steady state) at conditions quite different from those of the Phase 1 baseline conditions (i.e., deliberately scheduled for a time when the baseline might likely have shifted). Improved indicator relationships might be developed using the additional data, and these improved indicators might then replace the "temporary" indicators.

A number of alternatives can be considered for selecting "temporary" indicators. The individual parameter can be considered its own "temporary" indicator. Phase 2 monitoring would thus include the individual parameter itself (or perhaps the same survey techniques used in Phase 1). This approach might be useful, particularly when only a few parameters are not represented by indicators.

Another alternative is to select temporary indicators which are broadly representative of that class/group of substances which includes the parameter of interest. Some possible temporary indicators of this type are analytical techniques listed under the heading of "non-specific chemical analysis" in Table 4-21. Temporary indicators should be meaningful and should also have advantages over the Phase 1 survey technique for the parameter of interest. For example, the testing required to obtain temporary indicators should be cheaper and/or simpler than that for the parameter. Otherwise, there is no point to choosing an indicator instead of the parameter itself.

Each periodic Phase 1 repeat during Phase 2 would increase the number of Phase 1 measurements, and would possibly provide data at a baseline different from the Phase 1 baseline. Both of these factors increase the probability that suitable indicator/parameter relationships might be identified. The data should be reviewed after each Phase 1 repeat to identify whether any indicator/parameter correlations have become apparent with the new data set.

It is possible that--even after substantial additional data becomes available during Phase 2--no suitable parameter/indicator relationship will be found for some particular parameter(s). In these cases, the choice must be made concerning whether Phase 2 monitoring for this parameter should be continued indefinitely. Such a choice will be a function of several factors including:

- parameter level,
- importance, hazard, toxicity,
- cost of sampling/analysis,
- accuracy of analysis,
- variability of the parameter,
- the number of parameters for which no indicator relationships are apparent.

4.2.2.2 Methods for Conduct of Phase 2

The intent of Phase 2 is to track the total Phase 1 data base, using a limited number of indicators, and to repeat the pertinent portions of Phase 1 when an indicator excursion suggests that a shift in the Phase 1 baseline has occurred. Once indicators are selected, the key issues that need to be addressed in designing the Phase 2 program to achieve these goals are:

- the method by which the Phase 2 results are compared against the Phase 1 results for each indicator,
- the magnitude of the excursion in the Phase 2 indicator which is necessary before a repeat of Phase 1 is warranted for the parameters represented by that indicator in the stream for which the excursion occurred, and
- the frequency of the Phase 2 monitoring for each indicator.

These three issues--plus the number of measurements made during Phase 1 (the quality of the Phase 1 baseline)--can be related by statistical principles.

A number of statistical considerations must be factored into the resolution of the above interrelated issues. These statistical considerations, which must be determined for each site, include:

- the acceptable degree of risk of a Type I error (false positive); i.e., the risk of concluding that the Phase 1 baseline has shifted when in fact it has not. The concern about a false positive, of course, is that it would suggest that a Phase 1 repeat is necessary when in fact it is not. Suitable selections of the method for comparing Phase 1/Phase 2 results, the accepted magnitude of the Phase 2 excursion, and (in some cases) the number of Phase 1 measurements can control the risk of a Type I error.
- the acceptable degree of risk of a Type II error (false negative); i.e., the risk of concluding that the baseline remains at the Phase 1 level when in fact it has changed. Another way of phrasing this is, What is the desired "power" of this Phase 2 program, the level of confidence that it will indeed detect baseline shifts? As will be discussed later, Type II error can be controlled by the number (frequency) of Phase 2 samples, the number of Phase 1 samples in some cases, and other factors, depending upon the nature of the method selected for comparing the Phase 1/Phase 2 results.
- the desired sensitivity in detecting baseline shifts during Phase 2. How small a shift in the baseline should be detected? This sensitivity can be controlled by the number (frequency) of Phase 2 and Phase 1 samples.

The decisions concerning the issues and the considerations listed above, will be influenced by a variety of statistical and practical factors:

- the practical limitations on the number of Phase 1 samples (and hence limitations on the accuracy of the Phase 1 mean and standard deviation);

- the coefficients of variation of the various indicators; the higher this variation, the greater the number of Phase 1 and/or Phase 2 samples needed to control the Type II error.
- the significance of the indicator or parameter; the more important the substance, the more accurately it might be tracked.
- the complexity and cost of available sampling and analytical techniques; if a substance requires more difficult or expensive techniques, this fact could influence the selected Phase 2 frequency.
- the accuracy of the available sampling/analysis techniques (also reflected in the coefficient of variation, above).
- the precision of the statistical relationship between the indicator and the substances it represents. If the indicator relationship is weak, and if it is desired to use the indicator to track the represented substances with a certain power, it might be necessary to select a greater power for monitoring the indicator.

Thus, the selection of the most desirable monitoring frequencies is not a precise quantitative process. The ability to detect changes in the baseline parameter values is the primary factor affected by monitoring frequencies. The ability to detect changes is also influenced by the decision criteria used to detect baseline shifts.

The first decision that must be made in designing the Phase 2 program is the method that will be used to compare the Phase 2 and Phase 1 results. Several alternative methods, and variations of methods, are available. One key criterion in selecting a suitable method from the list of alternatives is the number of Phase 1 measurements that can be made (i.e., the accuracy with which the Phase 1 mean and the standard deviation are known). Ideally, it would be desirable to make a fairly large number of measurements during Phase 1, so that the mean and the standard deviation for a substance would be accurately known. For substances measured fairly frequently in Phase 1 (e.g., continuously or weekly), this will be possible. However, if the number of

Phase 1 samples is limited by practical considerations, methods utilizing small-sample theory might be necessary. The methods that will be discussed here are the following:

- control chart analyses (most effective when number of Phase 1 samples is large),
- t-test (number of Phase 1 samples is small),
- nonparametric procedure (no distribution model is appropriate)

The issues listed at the beginning of Section 4.2.2.2 are now discussed for each of these three alternative statistical methods for comparing the Phase 1 and Phase 2 results. Different Phase 1/Phase 2 comparison methods, different "acceptable" Phase 2 excursions, and different Phase 2 monitoring frequencies might be considered for different indicators, based upon differences in the practical number of Phase 1 samples, in the significance of the indicators, and other factors.

Control Chart Analysis

If the indicator involved is amenable to frequent Phase 1 monitoring (e.g., bi-weekly, weekly, or even more frequently)--so that 25-50, or even more, Phase 1 measurements are realistically possible--then a fairly accurate Phase 1 mean and standard deviation can be determined. In control chart analyses, a decision criterion is selected--e.g., 3σ -- and Phase 1 for an indicator is repeated once each time a single Phase 2 measurement of that indicator (or, if desired, the average of multiple Phase 2 measurements) varies from the Phase 1 mean by an amount greater than this decision criterion. This approach is statistically most reliable when the mean and the standard deviation are fairly accurately known. (Application of the control chart approach when only a limited number of Phase 1 measurements are available is discussed in Reference 4-38).

In this approach, the Type I error is controlled by the selection of the decision criterion (the size of the accepted Phase 2 excursion). The larger the excursion that is allowed in Phase 2, before conducting a Phase 1 repeat, the smaller will be the likelihood of a false positive (fewer "unnecessary" Phase 1 repeats) and the greater will be the likelihood of a Type II error (lower power or confidence). Thus, after selecting the decision criterion to control Type I error, Type II error is controlled by the selection of the Phase 2 monitoring frequency (number of Phase 2 samples). If a relatively large accepted excursion were selected in order to reduce the likelihood of false positives, then a higher Phase 2 monitoring frequency might be selected in order to compensate for the resulting risk of false negatives. The sensitivity of this approach in detecting baseline shifts for a given indicator depends upon the standard deviation (or the coefficient of variation) for that indicator, as measured in Phase 1, and upon the number of samples obtained in Phase 1 and Phase 2.

This approach is often used in traditional quality control applications. The formulas/procedures governing this approach are described in Reference 4-37.

In order to decide whether control chart analysis might be suitable for the Phase 2 program on a given indicator, the program designer should consider the following points:

- Is it reasonable to obtain a fairly large number of samples during Phase 1 (e.g., 25 to 50)? Without a minimum number of samples, the Phase 1 mean and standard deviation might not be known with sufficient accuracy to use this approach. (See Reference 4-38 for cases where the Phase 1 sample number is limited.)
- Is a distribution model appropriate for the substance (e.g., normal, lognormal)? The control chart approach requires the use of a distribution model. (In general, a distribution model can be selected if 25 to 50 Phase 1 measurements are made.)

If this approach were selected, a procedure that might be utilized in applying the approach could be as follows.

- Select the decision criterion which will provide an acceptable Type I error. Traditionally, a value of 3σ is employed in quality control applications (Reference 4-32). This value results in only a small chance of a Type I error (3 out of 1000), while providing a reasonable opportunity to reduce Type II errors through suitable selection of Phase 2 monitoring frequency/ sample numbers. By comparison, the use of a 2σ criterion would achieve a lower Type II error rate, but would result in a higher Type I error rate (up to about 5 %). The use of 4σ criterion would reduce the risk of Type I errors to a negligible value, but would result in poor power (large Type II errors). Accordingly, a decision criterion of 3σ seems reasonable. Phase 1 monitoring for the substances represented by an indicator in a given stream would be repeated during Phase 2 once each time a single measurement of that indicator varied from its Phase 1 mean by more than $\pm 3\sigma$.

- Select the number of Phase 2 samples (the sampling frequency) needed for each indicator in order to control the Type II error rate (achieve acceptable power) and obtain the desired sensitivity. The calculated sample number will depend upon the variability (standard deviation) of the individual indicator. The relationship among all of these variables is illustrated in Figure 4-4, which assumes that Type I error has been controlled by the selection of a 3σ decision criterion (and that the distribution is normal). This figure shows the power of the test (probability of detecting baseline shift) as a function of an index b/σ, which is the the baseline shift (desired sensitivity) divided by the standard deviation of the indicator. The effect of Phase 2 sample number is shown by a parametric series of curves. As an example of the use of this figure, if the Phase 1 mean for an indicator is represented by the symbol μ, suppose that it were decided that a baseline shift of 50% of the Phase 1 mean (i.e., a sensitivity of $b = 0.5\mu$) in an indicator having a coefficient of variation of 25% (i.e., $\sigma/\mu = 0.25$, or $\sigma = 0.25\mu$) should be detected with a power of 95% (likelihood of Type II error of 5%). Referring to Figure 4-4, for a value of $b/\sigma = 0.5\mu/0.25\mu = 2.0$, and for a 95% probability, it is apparent that 20 samples would be statistically necessary. In other words, if 20 Phase 2 measurements were made for this particular indicator, and if none of them varied from the Phase 1 mean by more than $\pm 3\sigma$, then one could be 95% confident that the Phase 1 baseline had in fact not varied by more than 50%. If it is desired to maintain this confidence on an annual basis, then the 20 Phase 2 measurements would need to be made in the period of one year, suggesting a bi-weekly frequency.

  Another manner of presenting this same information is presented in Table 4-23. In this table, the power (probability of detecting a baseline shift) is presented as a function of the desired sensitivity (shift in baseline mean) and the number of

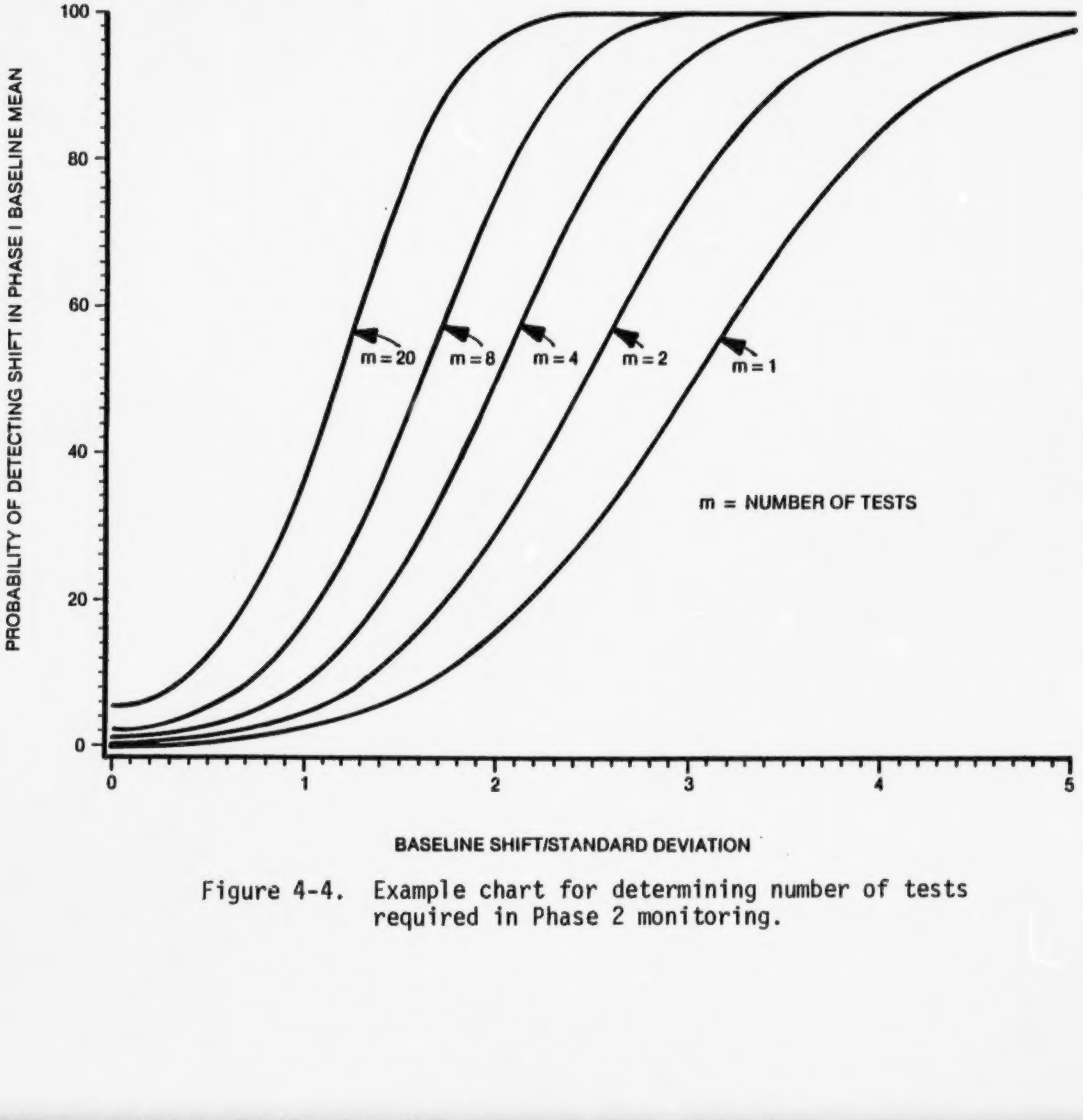

Figure 4-4. Example chart for determining number of tests required in Phase 2 monitoring.

samples, for the specific case of an indicator having a coefficient of variation of 50%. This table--which is designed to illustrate more clearly the effects of sensitivity in the selection of sample number--is derived directly from Figure 4-4, recognizing that the percentage baseline shift is 100 × b/μ, and the coefficient of variation is 100 × σ/μ. As an example of the meaning of the table, if one wished to detect a 100% shift from the Phase 1 baseline for this particular indicator, then one could only be 50% confident of detecting the shift if only 4 samples were taken (and were compared against the $\pm 3\sigma$) but one could be 97% confident if 20 samples were taken. Assuming again that it is desired to maintain this confidence on an annual basis, this example illustrates the impact upon power of a quarterly versus a biweekly sampling frequency.

Figure 4-4 and Table 4-23 (or comparable figures for, e.g., distributions other than normal decision criteria other than 3σ, etc.) can be used for the interrelated decisions concerning sample number, desired Type II error and desired sensitivity for a particular synfuels plant.

The power of this procedure also depends upon the number of indicator measurements made during each Phase 2 "test event". If a test event consists of multiple measurements--and if it is an average of these Phase 2 measurements that is compared against the Phase 1 mean--then the power of the procedure could be increased.

Since only one Phase 2 measurement would need to vary beyond the 3σ decision criterion in order to trigger a Phase 1 repeat for an indicator, by the example discussed in this section, it would be expected that the Phase 1 repeat would be conducted immediately, even if the excursion occurs before the full number of Phase 2 measurements is made. In such a case, the mean for the affected indicator would be recalculated based upon the data from the Phase 1 repeat, as discussed later; the Phase 2 monitoring would then "begin over again" using the new mean.

t-Test Procedure

The t-test is appropriate if either a normal or log-normal distribution model is known to apply for the indicator (or parameter) data (see Appendix B). In this approach, the average of the full set of measurements (2 or more) from the Phase 1 period are compared to the average of a set of measurements

TABLE 4-23. EXAMPLE APPLICATION OF FIGURE 4-4.

Number of Samples	Probability of Detecting a Shift in the Mean Baseline Value Within A Year of Occurrence			
	Percentage Shift of Baseline Mean			
	50% Shift	75% Shift	100% Shift	200% Shift
1	2%	7%	16%	84%
2	5%	13%	29%	97%
4	9%	24%	50%	99%
8	17%	42%	75%	100%
20	38%	75%	97%	100%

Coefficient of variation = 50%
Decision criterion = 3σ
Normal distribution model

(1 or more) from each Phase 2 sampling event. The t-statistic (Reference 4-39) is used to evaluate the statistical significance of the difference. The Type I error is controlled by the selection of the appropriate t-statistic. The Type II error is controlled by the sample size in Phase 1 and in each Phase 2 test event. Reference 4-40 can be used to evaluate the Type II error for alternative sample sizes in the two time periods.

The larger the sample sizes (number of measurements) in Phases 1 and 2, the greater the power of the test to detect differences between the means in the two periods. The basic assumptions of the t-test include 1) the distribution model is normal, 2) each measurement during Phase 1 and Phase 2 is independent or the others, and 3) the variability of the measurements is the same during Phase 1 as during Phase 2. If the log-normal distribution model is appropriate, then the data should be transformed (by taking logarithms of the measurements) prior to applying the test.

In making a decision to apply this test, the program designer should consider the following points:

1) Is the number of Phase 1 measurements limited to the point that the control chart analysis procedure might not be preferred?

2) Is it reasonable to assume the normal or lognormal model to describe the indicator data?

If the t-test is to be used, the user would need to make decisions concerning the following factors:

1) What are appropriate levels for the Type I and Type II errors (the t-statistic would be selected to provide the desired Type I error);

2) What magnitude of change in the mean level is it necessary to detect (i.e., what is desired sensitivity);

3) What number of measurements should be made during Phase 1, and what number during each Phase 2 test event, in order to achieve the desired Type II error and the desired sensitivity in detecting shifts;

4) Are data transformations needed; and

5) The frequency with which Phase 2 test events should occur, and the duration of each Phase 2 event (e.g., if Phase 2 samples from a given event are collected over a period of one week, the t-test would be comparing that Phase 2 week against the total Phase 1 period.).

In the t-test approach, each individual Phase 2 test event confirms the presence, or lack, of an excursion from Phase 1 within the designed Type I and Type II errors over the duration of the Phase 2 test event. The frequency with which Phase 2 events are conducted, therefore, depends upon how often the program designer wishes to check for a possible excursion.

One common approach is to select two as the number of measurements for each Phase 2 test event (the "two-sample t-test"). As an example of applying the two-sample t-test, suppose it were desired to maintain the Type I error at

5%, and the Type II error at 10%. Suppose, in addition that it were important to detect any excursion of greater than 100% from the Phase 1 mean each time a test event was done during Phase 2. If the coefficient of variation for the indicator of interest were 40% (and two measurements were made for each Phase 2 test event), then 23 measurements (samples) for that indicator would be necessary during Phase 1 to maintain the desired levels for the Type I and Type II errors.

Nonparametric Tests

If the number of Phase 1 measurements is limited, and if a data distribution model (e.g., normal or lognormal) for the parameter of interest is not known, then nonparametric tests may be appropriate to compare the results from Phase 2 with the results from Phase 1. As with the t-test, small sample nonparametric tests focus on changes in the indicator between Phases 1 and 2, rather than on the absolute value of the indicator. Nonparametric tests do not require strict assumptions on the form of a distribution model for the measurement data. In general, a nonparametric test will not be as powerful in detecting differences as a test which assumes a distribution model (such as the t-Test). Thus, if a distribution model is appropriate for the data, a test such as the Two-Sample t-Test should be used.

The nonparametric test can be applied to any number of measurements taken during Phase 1 and during each Phase 2 test event. Reference 4-41 includes a number of nonparametric test approaches which are appropriate for comparing Phase 2 results against Phase 1. Typically, the test criteria are based on percentiles (e.g., are the Phase 2 measurements from a single Phase 2 test event in the upper or lower quartile of the Phase 1 data, or above or below the Phase 1 median, etc.) or on order statistics (e.g., are all or some of the Phase 2 measurements from a single Phase 2 test event greater than the second-highest Phase 1 value, or below the minimum Phase 1 value, etc.). The Type I error is controlled by the selection of an appropriate critical value (tabulated) or by the selection of the particular percentile or order statistics. The Type II error is controlled by the sample sizes in Phase 1 and in each

Phase 2 test event. For most nonparametric tests it is not possible to quantify the Type II error without assuming a distribution model for the parameter (i.e. to quantify the magnitude of the excursion or mean drift).

In deciding whether to utilize nonparametric procedures, the program designer should consider the following:

1) Is the number of Phase 1 measurements limited to the point that the control chart analysis procedure might not be preferred?
2) Is the distribution model describing the indicator/paramater data uncertain? (These are the conditions under which nonparametric tests would be applied.)

If a nonparametric test is to be used to compare the Phase 1 and Phase 2 data, the user will need to make decisions concerning the following factors:

1) appropriate levels for Type I and Type II errors;
2) the type of changes from Phase 1 that one wishes to detect in the Phase 2 data (e.g., Is it desired to detect a shift in the Phase 1 mean?);
3) the direction of the changes that one wishes to detect in Phase 2 (e.g., just an upward shift of the mean, just a downward shift, or a shift in either direction);
4) the percentile or order statistic, and the number of samples in Phase 1 and in each Phase 2 test event, in order to achieve the desired Type I and Type II errors, and in order to detect the desired type and direction of changes in the Phase 2 data;
5) the frequency with which Phase 2 test events should occur and the duration of each Phase 2 event.

As in the t-test approach, each individual Phase 2 test event in the nonparametric approach confirms the presence, or lack, of an excursion from Phase 1 within the designed Type I and Type II errors over the duration of the Phase

2 test event. The frequency with which Phase 2 events are conducted, therefore, depends upon how often the program designer wishes to check for a possible excursion.

As a representative example of a nonparametric Phase 2 design, suppose that the order statistic is selected to be the second largest Phase 1 measurement for an indicator, the total number of Phase 1 measurements is 10, and the number of Phase 2 measurements is 2 for each test event. If a Phase 1 repeat is triggered only when both Phase 2 measurements exceed the second largest Phase 1 measurement, then one would be 90 percent confident (i.e., 10 percent chance of Type II error) that a Phase 1 repeat would in fact be triggered every time the mean for the indicator increased above the Phase 1 baseline by 2.8σ or more. In this example, there would be only a 5 percent chance of a Type I error (repeating Phase 1 when the baseline really had not shifted). In this example, the logistic distribution was used in defining the baseline shift of 2.8σ. Downward shifts in the baseline would not be detected in this example.

4.2.2.3 Updates of the Baseline Data Base

During the course of the Phase 2 monitoring program, data will be obtained which will enable the initial Phase 1 data base to be updated.

- Data will be obtained on a continuing basis for the indicators which were selected for Phase 2 monitoring.
- Data on parameters represented by certain indicators will be obtained occasionally when an excursion in those indicators suggests that the baseline has shifted for those indicators.
- One set of measurements for the total data base (Tables 4-4 through 4-6) might be repeated periodically, even if indicators do not experience excursions, to confirm that the data base has not dramatically shifted without this shift having been reflected by the indicators.

The manner in which the data from these sources might be used to update the Phase 1 data base is illustrated schematically in Figure 4-5.

Continuing Phase 2 data on indicators. The measurements of indicators that are made on a continuing basis throughout Phase 2 can be used to refine the baseline mean values and standard deviations for those indicators, based upon the increasing number of measurements. Statistical procedures to recompute the values are given in Appendix B.

Occasional data base monitoring triggered by indicator excursions. Occasional excursions will occur during Phase 2 in individual indicators in individual streams. If a Phase 2 excursion cannot be explained as being due to temporary, nonrepresentative variations in plant operation (e.g., equipment malfunction), the excursion should trigger one set of measurements for the substances represented by that indicator in that stream. Such a set of measurements would be conducted immediately after the indicator excursion is observed. This testing would effectively increase the Phase 1 data base (for the affected indicator and the parameters it represents) by one set of measurements. The results from each such set of measurements can be used as follows:

- For that indicator in that stream, one can now recalculate the relationship between the indicator and the parameter it represents. The uncertainty in the indicator/parameter relationship should be reduced, due to the increased number of "Phase 1" measurements now available. This improved certainty should enable an increased confidence (power) in tracking the various parameters using this indicator. Does the indicator/parameter relationship appear to be changing? Does it seem that some individual parameters are no longer represented well by this indicator? Are new indicator/parameter relationships apparent?

- Can the method of comparing Phase 1 and Phase 2 data be changed/improved with these additional data? For example, is it now possible to use the control chart approach rather than small sample theory for that indicator?

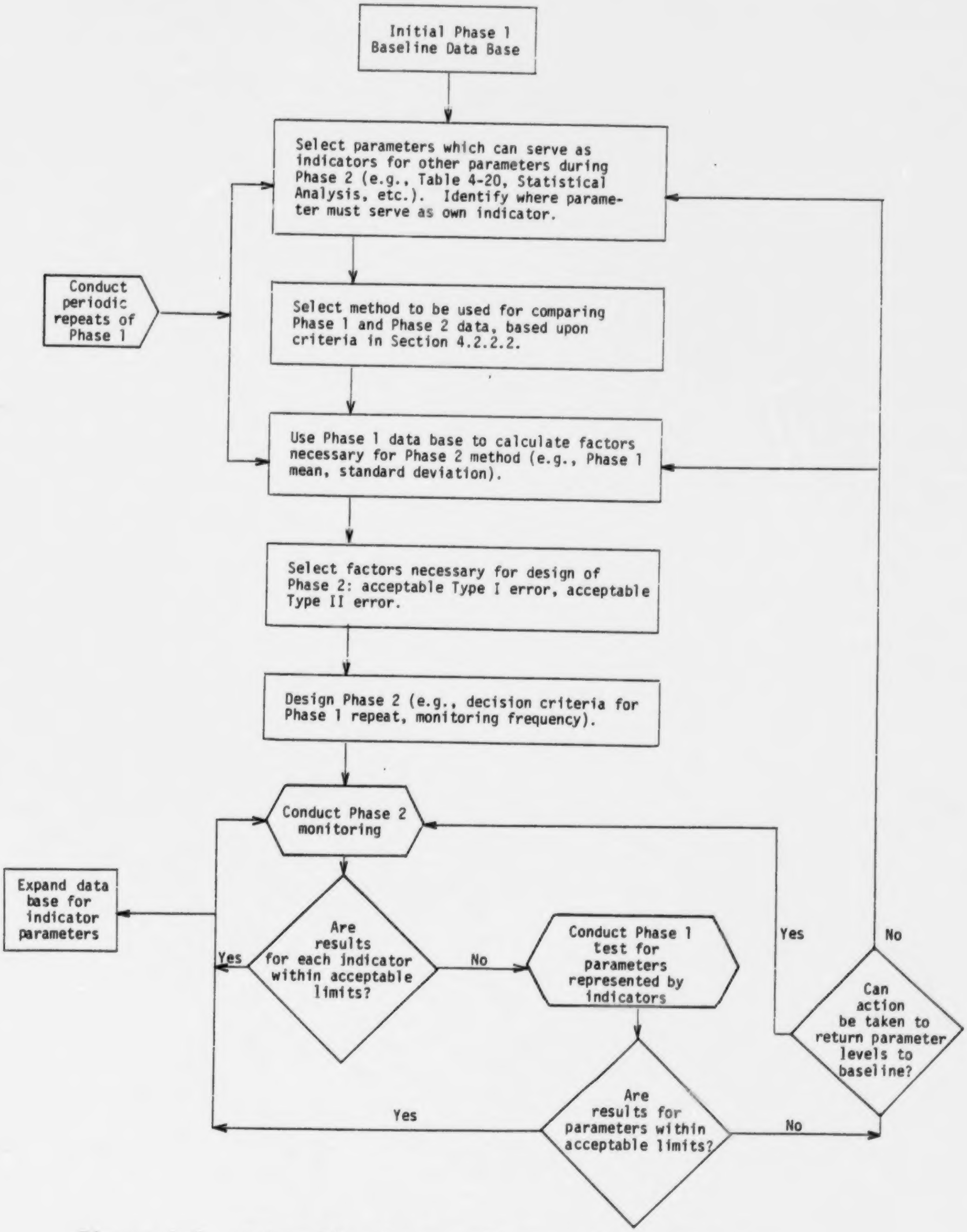
Initial Phase 1 Baseline Data Base
Select parameters which can serve as indicators for other parameters during Phase 2 (e.g., Table 4-20, Statistical Analysis, etc.). Identify where parameter must serve as own indicator.
Conduct periodic repeats of Phase 1
Select method to be used for comparing Phase 1 and Phase 2 data, based upon criteria in Section 4.2.2.2.
Use Phase 1 data base to calculate factors necessary for Phase 2 method (e.g., Phase 1 mean, standard deviation).
Select factors necessary for design of Phase 2: acceptable Type I error, acceptable Type II error.
Design Phase 2 (e.g., decision criteria for Phase 1 repeat, monitoring frequency).
Conduct Phase 2 monitoring
Expand data base for indicator parameters
Are results for each indicator within acceptable limits?
Yes
No
Conduct Phase 1 test for parameters represented by indicators
Yes
No
Can action be taken to return parameter levels to baseline?
Are results for parameters within acceptable limits?
Yes
No

Figure 4-5. Schematic diagram of approach for designing Phase 2 monitoring and updating Phase 1 data base.

- For that indicator, one can now recalculate the Phase 1 mean and standard deviation (or, e.g., the order statistic used in the nonparametric approach), and can use these new values in the continuation of Phase 2.
- Depending upon the impact of the new "Phase 1" results, it might now be practical to select, e.g., the reduced acceptable Type II error, because the increased number of Phase 1 samples could enable this reduced error to be achieved using a reasonable sample number/frequency.

Periodic repeats of total data base monitoring. Periodic repeats of monitoring for the total data base--consisting of one full set of the measurements listed in Tables 4-4 through 4-6--would be useful throughout Phase 2. Such periodic repeats would help indicate whether the baseline had in fact shifted without the indicators having varied outside of their selected limits. The frequency of such total data base repeats would be selected for the circumstances of the specific synfuels facility; the more variable the facility, the greater the variation in operating conditions (e.g., in feedstock, in product slate), the more frequent such repeats might be warranted. A frequency of approximately one repeat per year would seem generally reasonable. It might be useful to schedule such full repeats after major scheduled operating changes, because: a) that is when baseline shifts might logically be expected; b) that is when indicator excursions might most likely trigger repeats anyway; and c) obtaining additional data at such shifted conditions might improve the opportunity for defining indicator/parameter relationships, as discussed in connection with Figure 4-3.

The results from each total data base repeat can be used as follows:

- To improve the indicator/parameter relationships for all indicators in all streams, through the increased number of Phase 1 measurements now available. In particular, if the new data are at a different set of conditions (per Figure 4-3), current indicator/parameter correlations might be identified for parameters which were not previously represented by an indicator (other than the parameter itself). The validity of indicator/parameter correlations could be improved, and any changes in the relationship identified.

- To change/improve the method of Phase 1/Phase 2 data comparison, if possible (e.g., can the control chart approach now be used?).

- To recalculate the Phase 1 mean and standard deviation, etc., for use in the continuation of Phase 2.

- If warranted, to select new values for acceptable Type II errors.

4.3 ALTERNATIVE MONITORING APPROACHES

The phased monitoring program concept described in Section 4.2 represents one of a number of possible approaches that would satisfy the monitoring requirements of Section 131(e). In developing monitoring plans and outlines, SFC applicants might consider approaches different from the Section 4.2 approach. To illustrate the flexibility available in selecting the monitoring appraoch, the Section 4.2 approach and two alternative approaches are discussed in this section. The discussion focuses on the advantages and disadvantages of each approach and some of the issues to consider in selecting the most appropriate approach.

The intent of monitoring is to develop an information base that can be used to identify potential environmental problem areas. The monitoring program designed to accomplish this objective should be reasonable and cost-effective. The monitoring approach for a specific plant could depend upon a number of plant- and site-specific factors, such as:

- the extent and applicability of existing data on the processes proposed for use in the new facility. If much of the desired information base had already been addressed—e.g., through testing on earlier commercial-scale versions of the same process--this fact could influence the monitoring approach selected.
- the tradeoff between an increased data interpretation effort (for Phase 2 program design) versus an increased sampling/analysis effort in Phase 1. A phased approach will often permit a more confident characterization of the data base with a reduced total monitoring effort. However, this approach will require some judgment and interpretation of Phase 1 results in the design of Phase 2. If the data base were to be developed with a non-phased approach, less data interpretation would be needed, but the sampling/analysis effort might be greater. The cost-effectiveness of these tradeoffs would need to be considered on a case-by-case basis.

The monitoring approach described in Section 4.2 should be a responsive and cost-effective long-term approach for new synfuels facilities. Other approaches can satisfy the monitoring requirements, and might be preferred under various conditions. The three approaches discussed below are not a comprehensive compilation of all possible approaches. Rather, they are presented to indicate the flexibility available in selecting approaches. If an alternative approach is proposed in the monitoring plan for a specific plant, the test plan developer should evaluate how the results from the alternative approach would compare with those from the approaches described in this section. The plan should discuss how the results from the alternative approach will fill the data and information requirements of Section 131(e).

4.3.1 Option I - Phased Monitoring Approach Using Indicator Parameters in Phase 2

This is the approach described in Section 4.2. Phase 1 monitoring--conducted during the initial period of steady state plant operation--would develop a broad baseline data base using both survey analytical procedures and analyses for specific components. The survey procedures would screen for both regulated and unregulated chemical substances within selected classes, where these substances cannot be defined beforehand. In the design of Phase 2, the Phase 1 data would be statistically evaluated to select substances or parameters which might serve as "indicators" for the other substances/parameters observed during Phase 1. Monitoring during Phase 2 would proceed, addressing only the indicators. In theory, the entire baseline data base could thus be tracked during Phase 2 by monitoring a limited number of indicators. Phase 1 measurements (for the substances represented by a given indicator in a given stream) would be repeated during Phase 2 if an excursion of some predefined magnitude in that indicator suggested that the baseline had shifted.

Section 4.2 suggests the specific substances that might be monitored, and the survey analytical procedures that might be employed, in developing the Phase 1 baseline data base, together with the streams of possible interest.

The section also discusses the practical and statistical principles that can be used to select the indicators for Phase 2 and the monitoring frequency and duration for both phases. The frequency/duration would depend upon the desired accuracy of the results, including the accuracy of detecting baseline shifts during Phase 2.

This monitoring approach offers a number of advantages and disadvantages. The advantages include the following.

- The use of survey analytical procedures allows a broad data base to be effectively developed and avoids the need to guess which substances are going to be present. These survey procedures are particularly useful because commercial synfuels streams have not been well characterized and might contain a wide array of substances.
- The phasing concept enables a significant reduction in the monitoring effort after the first phase and still provides a broad data base. Long term monitoring is effectively focused on the substances actually present.
- The use of indicators allows the entire data base to be tracked throughout Phase 2, while greatly reducing the Phase 2 monitoring effort and eliminating the need for decisions about which of the substances observed in Phase 1 warrant continued monitoring.
- The application of statistical principles in selecting Phase 1 measurement frequency and designing Phase 2 would provide a defensible data base with known accuracy.

There are also several potential disadvantages associated with this approach.

- The phasing concept necessarily delays design of part of the monitoring program (the extended Phase 2 portion) until after Phase 1 is completed. This factor prevents a complete definition of scope and duration at the outset of the monitoring program.
- The Phase 2 design could require a fair degree of statistical data interpretation following Phase 1. A mechanism for making decisions at the end of Phase 1 is also required.

- The Phase 1 results might not provide an adequate relationship between some of the observed substances and potential indicators for those substances. If a good indicator relationship is not apparent for some substances from the Phase 1 data, it might be necessary to continue monitoring for those substances during Phase 2.

- A baseline shift might occur during Phase 2 without a simultaneous excursion in Phase 2 indicators. The risk of occurrence depends on the strength of the relationship between the indicator and the represented substances and on the statistical design of the monitoring program (the sensitivity in detecting baseline shifts). To guard against such undetected shifts, Section 4.2 suggests that Phase 1 monitoring be repeated periodically throughout Phase 2.

4.3.2 Option II - Phased Monitoring Approach with Deletions Following Phase 1

In this approach, Phase 1 would proceed as described for Option I above. However, the Phase 1 results would be interpreted differently in the design of Phase 2. Rather than using Phase 1 results to select indicators, the results would be used to decide which of the substances observed in Phase 1 should continue to be monitored during Phase 2. Phase 2 would then address only those substances which were both a) observed during Phase 1, and b) felt to be present at levels significant enough to warrant extended monitoring.

A major issue in this approach is the method for deciding which of the measurements are "significant." The criteria for establishing significance would need to be defined in the monitoring plan. Examples of factors to consider include the concentration at which the substance was observed, the consistency with which it was observed, the presence of the substance on recognized pollutant lists and the potential health and ecological effects of the substance (e.g., toxicity, mutagenicity, tendency for bioaccumulation, etc.). "Trigger values"--concentrations which, if exceeded in Phase 1, would trigger monitoring for a given substance during Phase 2--might be agreed upon.

The major advantages of this monitoring approach are as follows.

- The use of survey analytical procedures allows a broad data base to be collected under conditions where the composition is not well understood beforehand, as in Option I above.
- The use of phasing should allow a significant long-term reduction in, and focusing of, the monitoring effort, as in Option I.
- There is no need to identify Phase 2 indicators, so the risk of being unable to define suitable indicators for some substances is avoided, as is the statistical effort required to define the indicators.
- Statistical principles can be employed to provide a defensible data base.

Some potential disadvantages of this approach are:

- The use of phasing prevents the Phase 2 part of the program from being defined until Phase 1 is completed, as in Option I.
- A mechanism and criteria for decisions concerning Phase 2 design at the end of Phase 1 will be necessary, although less statistical analysis might be required in comparison with Option I.
- Judgments about the "significance" of the various substances observed during Phase 1 would be required for the Phase 2 design. The decision concerning which Phase 1 substances warrant continued monitoring would likely require a fair amount of evaluation. One option might be that Phase 2 would address every substance seen above detection limits during Phase 1. This approach would eliminate the requirement for judgments about significance, but could result in a relatively large Phase 2 program.
- The Phase 2 effort might not address the total baseline (Phase 1) data base. If the substances deemed "significant" cover only a portion of the data base, the Phase 2 monitoring would not provide information on changes in the other portion of the data base. Therefore, it would be useful (as in Option I) to repeat the full Phase 1 program periodically to confirm that baseline shifts are not causing discharges of other "significant" substances.

4.3.3 Option III - Non-Phased Monitoring Approach: Continued Survey

In this non-phased approach, monitoring of all Phase 1 parameters would continue with no attempt to reduce monitoring as results became available. The repeated monitoring of the total data base would include survey analytical techniques and specific component analyses as used in the first two "phased" approaches. In this, however, "Phase 1" monitoring would continue for some extended period, with no attempt to design a reduced Phase 2.

This non-phased approach would produce a more comprehensive data set than the phased approaches, because the total "Phase 1" monitoring effort would be continued for an extended period while the other two approaches call for a reduced Phase 2. In view of this more comprehensive data set, it might be possible to conclude the non-phased monitoring effort at an earlier time than either of the phased approaches might be concluded. (The total duration of the monitoring program must be acceptable to the SFC and other consulting agencies.) In any case, it should be of adequate duration to establish a complete data history, addressing a broad range of plant conditions.

The non-phased approach offers several advantages.

- The use of survey analytical procedures allows a broad data base to be collected under conditions where stream properties are not well known beforehand, as in Options I and II above.
- Since no changes will be made in the monitoring program after it is initiated (i.e., a Phase 2 program will not be designed after a Phase 1 is completed), the exact nature of the total monitoring program can be defined at the outset.
- Potential difficulties associated with the design of a Phase 2 program are avoided; i.e., no extensive statistical Phase 1 data interpretation/Phase 2 design, no uncertainties concerning the selection of indicators, no judgments required concerning which observed substances are "significant," etc.

- This option provides the most comprehensive data set, since simplifying assumptions (e.g., regarding the ability of a limited number of indicators to track the total data base, as in Option I) are not required. The total data base is monitored repeatedly.

This approach has two major disadvantages:

- Since no attempt is made to reduce the monitoring effort based on the initial results, this approach could result in a more substantial and expensive monitoring effort.
- If the duration of monitoring under Option III is less that that under Options I or II, then Option III would not provide the longer-term coverage features of the other approaches. Such features allow detection of significant shifts in the plant operating baseline, so that additional monitoring data can be gathered.

4.4 MONITORING PROCEDURES

In Tables 4-4 through 4-6 (Section 4.1.2), general analytical procedures and specific components were suggested for the monitoring data base. As a result of Phase 1 monitoring, indicators such as those listed in Tables 4-20 and 4-21 might be selected for monitoring in Phase 2. This section outlines monitoring procedures that might be considered for conducting Phase 1 and Phase 2.

Tables 4-24 through 4-26 (included at the end of this section) present specific procedures which are suggested for the Phase 1 survey analytical techniques referenced in Tables 4-4 through 4-6 (for gaseous, aqueous and solid streams). Tables 4-27 through 4-29 (also at the end of this section) list alternative techniques for:

- the specific components listed in Tables 4-4 through 4-6
- additional components that may be monitored,
- those compounds from which Phase 2 indicators are expected to be selected, and
- alternative Phase 1 survey analytical techniques (in addition to those given in Tables 4-24 through 4-26).

The commonly applicable techniques are marked in Tables 4-27 through 29 with an asterisk. If any of the Phase 1 techniques suggested in Tables 4-24 through 4-26 are not applicable in a specific synfuels plant, Tables 4-27 through 4-29 are a starting point for alternative technique selection.

The procedures listed in Tables 4-24 through 4-29 are described in further detail in Appendix A. Each entry in the tables includes an index term, which involves a letter (S for sampling method, P for preservation and preparation methods, A for analytical method and T for test method) and two digits; this index term can be used to locate the more detailed discussion of the method in Appendix A. In the Appendix, the S entries are presented first, the P entries second, and so on.

The procedures in the tables are broken down according to three major steps: sampling, sample preservation/preparation, and analysis or testing. Often, the steps in the monitoring sequence are linked in a specific manner (e.g., specific analyses requires specific sample preparation method). These linkages are shown in the tables.

The information presented reflects the key elements of each sampling, preservation/preparation, and analysis or test procedure. Further detail would be necessary for the procedure to be implemented; for example, what pH or what solvent might be used for an extraction, or what sample volume is needed for the desired sensitivity. These details must be defined as part of a specific monitoring program and will depend upon the circumstances associated with specific samples. The procedural constraints which influence these details are discussed in Appendix A.

4.4.1 Suggested Phase I Survey Techniques

The suggested Phase 1 survey techniques in Tables 4-24 through 4-26 were selected to provide the broadest coverage of a wide array of potential components, using the most limited number of procedures. These techniques are presented in the same format as they appeared in the corresponding Tables 4-4 through 4-6. Also shown in Tables 4-24 through 26 are the generic stream categories for which the technique was suggested in Tables 4-4 through 4-6. In general, for each group of components of interest, one sampling method, one preservation/preparation method and one analytical method are shown, constituting a suggested approach. Where multiple entries are shown, the meaning is as follows.

- volatile versus non-volatile organics--although a single entry is shown for organic survey techniques in Tables 4-4 through 4-6, this single entry requires two approaches: one for volatile compounds, and one for non-volatile compounds. The techniques for volatile versus non-volatile usually differ slightly (i.e., sample collection techniques vary, therefore preservation/preparation techniques are different).

- multiple entries under sample preparation--where more than one preparation technique is listed, each preservation/ preparation step is often necessary and they are generally executed in the order listed.
- multiple entries under analytical method--where more than one analytical technique is listed, each analytical procedure is often necessary to obtain useful information for a monitoring data base. The procedures are listed in order of increasing specificity and most often are performed in the sequence shown.

Although the techniques suggested in Tables 4-24 through 4-26 will be reasonable selections, there might be circumstances under which one or more of these techniques is not be applicable. The sampling conditions (temperatures, pressures, etc.) and the stream compositions (with resulting analytical interferences) will vary significantly from one plant to the next. Accordingly, in some cases, alternative techniques will need to be selected. Alternatives might be selected from Tables 4-27 through 4-29. For example, if a sample contains non-volatile components that are not amenable to gas chromatography (e.g., GC/MS) then a HPLC technique might be used instead.

4.4.2 Alternative Techniques

Tables 4-27 through 4-29 list alternative procedures that might be considered for the full array of monitoring: techniques for individual Phase 1 components; alternative techniques for Phase 1 surveys; and techniques for Phase 2 indicators. Some of the listed methods are for components currently regulated in other industries, and/or are EPA reference methods or, APHA or ASTM methods. Where a technique can be implemented with a commonly-known procedure such as an EPA reference method, this fact is indicated in the referenced procedure in Appendix A. Although all of the techniques listed for monitoring could be appropriate under various circumstances, the commonly applicable techniques are marked with an asterisk.

In Tables 4-27 through 4-29, the listings for individual substances (such as SO_2, H_2S, etc.) include both grab sample approaches and indicate available continuous monitoring. Continuous monitoring will often be the most cost-effective approach if the necessary sampling/analysis frequency is high.

If Tables 4-27 through 4-29 are used to select a procedure for monitoring a Phase 2 indicator, it would be necessary to identify the component or class to which the particular indicator belongs. For example, if the particular indicator is a non-volatile oxygenate in an aqueous stream, the user would review the procedures listed for non-volatile oxygenates in Table 4-28. Knowing the specific indicator compound of interest, and knowing the other (potentially interfering) compounds present in the stream, the experienced analyst could select a set of suitable procedures from the list of alternatives. Then the operating details could be determined to tailor the approach to define the compound of interest most effectively. The selected procedure for the Phase 2 indicator probably could be related to the Phase 1 technique (for oxygenates in this example). Generally, with the technique aimed at a specific compound, it would be determined more reliably. Potentially, the cost of implementation would be less than the Phase 1 approach.

If a Phase 1 survey technique different from those listed in Tables 4-24 to 4-26 is needed, the appropriate component or class in Tables 4-27 through 4-29 would be referenced. The experienced analyst could select from the Table 4-27 alternatives, a technique which would circumvent the difficulty encountered with the Table 4-24 approach. For example, if the Table 4-24 sampling technique for volatile nitrogen compounds (Tenax resin) is not appropriate in a specific gas stream, then one would review the alternatives for volatile nitrogen compounds in Table 4-27. After reviewing the descriptions in Appendix A and the references cited, one might select trapping on charcoal. In this example, if charcoal were selected, the sample probably would be solvent extracted (different preparation step from that for Tenax) and analyzed by GC/MS and/or GC with a nitrogen specific detector (a variation on the analysis step in Table 4-24).

While the techniques listed in Tables 4-24 through 4-29 are conventional procedures in common usage, their applicability to a specific synfuels stream might vary, depending upon a number of factors (the best example being stream composition, which could lead to interferences from other components in the stream). Accordingly, method evaluation and verification should be performed during the plant startup period, as discussed in Section 3.4 and 4.2.1.3. This evaluation/verification would be one component of a good sampling and analytical quality assurance program. Although historical data on limitations and interferences are available for the methods in the tables, some of these analyses will be employed in matrices different from those on which historical data are available. Some modification of existing methods might be needed.

One issue of particular interest is the sensitivity with which the components are detected. For many techniques, sensitivity depends on implementation and sample size. For example, if a large aqueous sample is taken and extracted for organics, the organic compounds will be detected with a greater sensitivity than if a smaller aliquot were extracted. This issue is discussed further at the beginning of Appendix A (see Table A-1). Because of the potential variation in sensitivity, the sensitivity figures in Appendix A are often presented as a range.

TABLE 4-24. SUGGESTED PHASE 1 SURVEY TECHNIQUES FOR GASEOUS STREAMS*

Survey Technique (Listed in Table 4-4)	Generic Stream	Sampling	Preparation	Analysis or Test
Analysis for Trace Elements	2, 3	Impinger (S07D)	Acidic preservation (P11) and Acid digestion (P12)	AA (A40) for As, Sb, Se, Hg. ICP (A40) for other elements of interest
Analysis for Aliphatics and Aromatics	2			
- Volatile	5	Tenax sorbent resin (S05)	Thermal desorption (P03)	GC/MS (A11)^{a,b}
- Condensable		XAD-2 sorbent resin (S05)	Cool (P11) and extract (P01) both sorbent and condensate, followed by LC fractionation (P05)^{c}	TCO (A12)+GRAV (A13)^{d} and GC/MS (A11) and GC-PID (A19)^{b}
Analysis for Aliphatics, Aromatics and Oxygenates	3,4			
- Volatile		Tenax sorbent resin (S05)	Thermal desorption (P03)	GC/MS (A11)^{a,b}
- Condensable		XAD-2 sorbent resin (S05)	Cool (P11) and extract (P10) both sorbent and condensate, followed by LC fractionation (P05)^{c}	TCO (A12)+GRAV (A13)^{d} and GC/MS (A11) and GC-PID (A19)^{b}

(Continued)

TABLE 4-24. (continued)

Survey Technique (Listed in Table 4-4)	Generic Stream	Sampling	Preparation	Analysis or Test
Analysis for Nitrogenous Compounds	2, 3			
- Volatile		Tenax sorbent resin (S05)	Thermal desorption (P03)	GC/MS (A11)[a,e]
- Condensable		XAD-2 sorbent resin (S05)	Cool (P11) and extract (P01) both sorbent and condensate, followed by fractionation (P05)[c]	TCO (A12)+GRAV (A13)[d] and GC/MS (A11) and GC-N specific (A10)[e]
Analysis for Sulfur Containing Compounds	3			
- Volatile		Tenax sorbent resin (S05)	Thermal desorption (P03)	GC/MS (A11)[a,f]
- Condensable		XAD-2 sorbent resin (S05)	cool (P11) and extract (P01) both sorbent and condensate, followed by LC fractionation (P05)[c]	TCO (A12)+GRAV (A13)[d] and GC/MS (A11) and GC-S specific (A18)[f]

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[*] For survey analysis of entrained particulate, see solids techniques in Table 4-26.

[a] Analysis of Tenax resin aliquots is often hampered by contamination during homogenation and aliquot preparation. Therefore, multiple analysis techniques are not recommended.

[b] Although GC-PID is often more sensitive for the detection of simple aromatics; if compound confirmation is desired, GC/MS is the more appropriate technique.

[c] Fractionation may be appropriate for complex samples. Fraction or fractions of interest can be selected prior to analysis. If capillary GC is implemented, fractionation will be necessary less frequently.

[d] TCO and GRAV or TCO may be useful to determine organic loading prior to specific analyses.

[e] Although GC-N specific (HECD-N or NPD) is often more sensitive for the detection of nitrogenous compounds; if compound confirmation is desired, GC/MS is the more appropriate technique.

[f] Although GC-S specific (HECD-S or FPD) is often more sensitive for the detection of the sulfur containing compounds; if compound confirmation is desired, GC/MS is the more appropriate technique.

TABLE 4-25. SUGGESTED PHASE 1 SURVEY TECHNIQUES FOR AQUEOUS STREAMS

Survey Technique (Listed in Table 4-5)	Generic Stream	Sampling	Preparation	Analysis or Test
Analysis for Trace Elements	1,2, 3, 4	Composite (S10)	Acidic preservation (P11) and acid digestion (P12)	AA (A40) for As, Sb, Se, Hg. ICP (A40) for other elements of interest
Analysis for Aliphatics and Aromatics	1,4			
- Volatile		Grab (S11)	Cool (P11), purge and trap (P03)	GC/MS (A11)^{a,b}
- Extractable		Composite (S10)	Cool (P11), extraction (P01), base/neutral extract followed by LC fractionation (P05)^e	TCO (A12)+GRAV (A13)^c and GC/MS (A11) and GC-PID (A19)^b
Analysis for Aliphatics, Aromatics and Oxygenates	3			
- Volatile		Grab (S11)	Cool (P11), purge and trap (P03)	GC/MS (A11)^{a,b}
- Extractables		Composite (S10)	Cool (P11), extraction (P01) acid extract analyzed for phenols and carboxylic acids^c. Base/neutral extract followed by LC fractionation (P05)^e	TCO (A12)+GRAV (A13)^c and GC/MS (A11) and GC-PID (A19)^b

(Continued)

TABLE 4-25. (continued)

Survey Technique (Listed in Table 4-5)	Generic Stream	Sampling	Preparation	Analysis or Test
Analysis for Nitrogenous Compounds	3			
- Volatile		Grab (S11)	Cool (P11), purge and trap (P03)	GC/MS (A11)^{a,f}
- Extractable		Composite (S10)	Cool (P11), extraction (P01), base/neutral extract^{d} followed by LC fractionation (P05)^{e}	TCO (A12)+GRAV (A13)^{c} and GC/MS (A11) and GC-N specific (A10)^{g}
Analysis for Sulfur Containing Compounds	3			
- Volatile		Grab (S11)	Cool (P11), purge and trap (P03)	GC/MS (A11)^{a,g}
- Condensable		Composite (S10)	Cool (P11), extraction (P01), base/neutral extraction followed by LC fractionation (P05)^{e}	TCO (A12)+GRAV (A13)^{c} and GC/MS (A11) and GC-S specific (A18)^{h}

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[a] Aliquots of samples for volatile organic analysis by purge and trap techniques are not appropriate. Therefore, multiple analysis techniques are not recommended.

[b] Although GC-PID is often more sensitive for the detection of simple aromatics, if compound confirmation is desired, GC/MS is the more appropriate technique.

[c] TCO and GRAV or TCO may be useful to determine organic loading prior to specific analyses.

[d] Phenols can be analyzed directly with appropriate GC column selection. Carboxylic acids may require derivitization to be chromatographable.

[e] Fractionation may be appropriate for complex samples. Fraction or fractions of interest can be selected prior to analysis. If capillary GC is implemented, fractionation will be necessary less frequently.

[f] Many nitrogenous compounds are chromatographable without derivitization with appropriate GC column selection.

[g] Although GC-N specific (HECD-N or NPD) is often more sensitive for the detection of nitrogenous compounds; if compound confirmation is desired, GC/MS is the more appropriate technique.

[h] Although GC-S specific (HECD-S or FPD) is often more sensitive for the detection of sulfur containing compounds; if compound confirmation is desired, GC/MS is the more appropriate technique.

TABLE 4-26. SUGGESTED PHASE 1 SURVEY TECHNIQUES FOR SOLID STREAMS

Survey Technique (Listed in Table 4-6)	Generic Stream	Sampling	Preparation	Analysis or Test
Analysis for Trace Elements	1, 2, 3, 4			
- Whole sample		Composite (S01)	Fusion (P09) and/or acid digestion (P10)	AA (A40) for As, Sb, Se, Hg. ICP (A40) for other elements of interest
- Leachable		(Leachate)	Acidic preservation (P11) and acid digestion (P12)	AA (A40) for As, Sb, Se, Hg. ICP (A40) for other elements of interest
Analysis for Leachable Aliphatics and Aromatics	1			
- Volatile		(Leachate)	**	**
- Extractable		(Leachate)	Cool (P11), extraction (P01) followed by LC fractionation (P05) on base/neutral extract[a]	TCO (A12)+GRAV (A13)[b] and GC/MS (A11) and GC-PID (A19)[c]
Analysis for Extractable* Aliphatics and Aromatics	4	Composite (S01)	Extraction (P01), followed by LC fractionation (P05) on base/neutral extract[a]	TCO (A12)+GRAV (A13)[b] and GC/MS (A11) and GC-PID (A19)[c]
Analysis for Leachable Aliphatics, Aromatics and Oxygenates	3			
- Volatile		(Leachate)	**.	**
- Extractable		(Leachate)	Cool (P11), extraction (P01), Acid Extract analyzed for phenols and carboxylic acids.[a] Base/neutral extract followed by LC fractionation (P05)[a]	TCO (A12)+GRAV (A13)[b] and GC/MS (A11) and GC-PID (A19)[c]

(Continued)

TABLE 4-26. (continued)

Survey Technique (Listed in Table 4-6)	Generic Stream	Sampling	Preparation	Analysis or Test
Analysis for Extractable* Aliphatics, Aromatics and Oxygenates	3	Composite (S01)	Extraction (P01), acid extract analyzed for phenols and carboxylic acids[e]. Base/neutral extract followed by LC fractionation (P05)[a]	TCO (A12)+GRAV (A13)[b] and GC/MS (A11) and GC-PID (A19)[c]
Analysis for Leachable Nitrogen Containing Compounds	3			
- Volatile		(Leachate)	**	**
- Extractables		(Leachate)	Cool (P11), extraction (P01), LC fractionation (P05) on base/neutral extract[a,f]	TCO (A12)+GRAV (A13)[b] and GC/MS (A11) and GC-N specific (A10)[d]
Analysis for Extractable* Nitrogen Containing Compounds	3	Composite (S01)	Extraction (P01), LC fractionation on (P05) base/neutral extract[a,f]	TCO (A12)+GRAV (A13)[b] and GC/MS (A11) and GC/N specific (A10)[d]
Analysis for Leachable Sulfur Containing Compounds	3			
- Volatile		(Leachate)	**	**
- Extractable		(Leachate)	Cool (P11), Extraction (P01), followed by LC fractionation on base/neutral extract[a]	TCO(A12)+GRAV (A13)[b] and GC/MS (A11) and GC-S specific (A18)[g]

(Continued)

TABLE 4-26. (continued)

Survey Technique (Listed in Table 4-6)	Generic Stream	Sampling	Preparation	Analysis or Test
Analysis for Extractable* Sulfur Containing Compounds	3	Composite (S01)	Extraction (P01), followed by LC fractionation on base/neutral extract[a]	TCO (A12)+GRAV (A13)[b] and GC/MS (A11) and GC-S specific (A18)[g]

[*] Purging or thermal desorption techniques, which define volatile organic fractions for liquids or gases, are not generally appropriate for solids. Therefore, no volatile classification is shown.

[**] Analysis for volatile organics present in a leachate would follow the same suggested guidelines as for volatile organics from aqueous streams (see Table 4-25). However, if volatiles remain in the solid waste and are leached, they would most likely be lost during the leaching procedure.

[a] Fractionation may be appropriate for complex samples. Fraction or fractions of interest can be selected prior to analysis. If capillary GC is implemented, fractionation will be necessary less frequently.

[b] TCO and GRAV or TCO may be useful to determine organic loading prior to specific analyses.

[c] Although GC-PID is often more sensitive for the detection of simple aromatics; if compound confirmation is desired, GC/MS is the more appropriate technique.

[d] Although GC-N specific (HECD-N or NPD) is often more selective for nitrogenous compounds, if compound confirmation is desired, GC/MS is the more appropriate technique.

[e] Phenols can be analyzed directly with appropriate GC column selection. Carboxylic acids may require derivitization to be chromatographable.

[f] Many nitrogenous compounds are chromatographable without derivitization with appropriate GC column selection.

[g] Although GC-S specific (HECD-S or FPD) is often more selective for sulfur containing compounds; if compound confirmation is desired, GC/MS is the more appropriate technique.

TABLE 4-27. MONITORING OPTIONS FOR GASEOUS STREAMS

Property or Specie	Generic Stream	Sampling Options	Preparation Options	Analysis or Test Options
Major Gases				
CO	1,2,3	continuous monitoring, or		
		gas bomb* or bag (S13)	part/aerosol removal(S06) +H_2O removal (S04)* or	GC-TCD(A03)*
			part/aerosol removal(S06)	orsat(A03)
	5	screening(S12)* or	NA	detector tubes(S12)*
		bagging(S14)+ gas bomb(S13)	NA	GC-TCD(A03)
H_2	1,2,3	gas bomb* or bag (S13)	part/aerosol removal(S06) +H_2O removal(S04)* or	GC-TCD(A03)*
			part/aerosol removal(S06)	orsat(A03)
CO_2	1,2,3	continuous monitoring, or		
		gas bomb* or bag(S13)	part/aerosol removal(S06) +H_2O removal (S04)* or,	GC-TCD(A03)*
			part/aerosol removal(S06)	GC-TCD(A03)
N_2	1,2,3	gas bomb* or bag(S13)	part/aerosol removal(S06) +H_2O removal(S04)*	GC-TCD(A03)
		gas bomb(S13)	part/aerosol removal(S06)	orsat(A03)
O_2	1,2,3	continuous monitoring, or		
		gas bomb* or bag(S13)	part/aerosol removal(S06) +H_2O removal(S04)*, or	GC-TCD(A03)*
			part/aerosol removal(S06)	orsat(A03)
CH_4	1,2,3	continuous monitoring, or		
		gas bomb* or bag(S13)	part/aerosol removal(S06) +H_2O removal(S04)* or	GC-TCD(A03)*, or GC-FID(A02)*
			part/aerosol removal(S06)	orsat(A03)
	5	screening(S08)*, or	NA	portable FID(S08)*
		bagging(S14)+ gas bomb (S13)	NA	GC-FID(A02)
Moisture	1,2,3,4	Silica gel(S02)*	part/aerosol removal(S06)*	gravimetric(S02)*

(Continued)

TABLE 4-27. (continued)

Property or Specie	Generic Stream	Sampling Options	Preparation Options	Analysis or Test Options
Sulfur Gases				
SO_2	1,2	continuous monitoring, or		
		impinger(S07F)*	cool(P11)part/aerosol removal(S06)*	turbidimetric $SO_4^=$(A35)*
	1,2,3,4	gas bomb* or bag(S13)	part/aerosol removal(S06) +H_2O removal(S04)*	GC-FPU(A01)* or GC-TCD(A03)
H_2S	2,3,4,6	continuous monitoring, or		
		impinger(S07E)*, or	filter(P11), + part/aerosol removal(S06)*	titration $S^=$(A29)*
		gas bomb or bag (S13)	part/aerosol removal(S06) +H_2O removal (S04)	GC-FPU(A01) or GC-TCD(A03)
	5	screening(S12)*, or	NA	detector tubes(S12)*
		bagging(S14) + gas bomb (S13)	NA	GC-FPD(A01)
COS	2,3,4,6	gas bomb* or bag(S13)	part/aerosol removal(S06) +H_2O removal(S04)*	GC-FPU(A01)*
	5	bagging(S14)+ gas bomb(S13)*	part/aerosol removal(S06)*	GC-FPD(A01)*
CS_2	2,3,4,6	gas bomb* or bag(S13)	part/aerosol removal(S06) +H_2O removal(S04)*	GC-FPU(A01)*
	5	bagging(S14)+ gas bomb(S13)*	NA	GC-FPD(A01)*
Mercaptans	2,3,4,6	gas bomb* or bag(S13)	part/aerosol removal(S06) +H_2O removal(S04)*	GC-FPU(A01)*
	5	bagging(S14)+ gas bomb(S13)*	NA	GC-FPU(A01)*

(Continued)

TABLE 4-27. (continued)

Property or Specie	Generic Stream	Sampling Options	Preparation Options	Analysis or Test Options
Nitrogen Gases				
NH_3	2,3,4,6	impinger(S07B)*	part/aerosol removal(S06) +acidic,cool(P11)*	titration NH_4^+(A27)*
		gas bomb or bag(S13)	part/aerosol removal(S06) + H_2O removal(S04)	GC-TCD(A03)
	5	bagging(S14)+impinger (S07B), or	acidic,cool(P11)	titration NH_4^+(A27)
		screening(S12)*	NA	detector tubes(S12)*
HCN	2,3,4,6	impinger(S07A)*	part/aerosol removal(S06) +basic, cool(P11)*	colorimetric CN^-(A28)*
	5	bagging(S14)+ impinger(S07A), or	part/aerosol removal(S06) +basic, cool(P11)	colorimetric CN^- (A28)
		screening(S12)*	NA	detector tubes(S12)*
NO_x	1,2,3	continuous monitoring, or		
		impinger(S07C)*	part/aerosol removal(S06)*	spectrometric(A41)*
Halogen Gases				
HF	1,2,3	impinger(S07H)*	part/aerosol removal(S06)*	SIE F^-(A31)*
HCl	1,2,3	impinger(S07G)*	part/aerosol removal(S06)*	potentiometric Cl^-(A33)*
Particles/Aerosols				
Opacity	1,2,3	continuous monitoring, or		
		NA	NA	visual determination(T21)*
Loading	1,2,3	isokinetic(S03)*	NA	gravimetric(S03)*
	6,7	high vol(S15)*	NA	gravimetric(S15)*
Size Distribution	1,2,3	isokinetic(S03)*	NA	gravimetric(S03)*, or microscopy(A08)
	6,7	high vol(S15)*	NA	gravimetric(S15)*, or microscopy(A08)
Composition	1,2,3	isokinetic(S03)*	**	**
	6,7	high vol(S15)*	**	**

(Continued)

TABLE 4-27. (continued)

Property or Specie	Generic Stream	Sampling Options	Preparation Options	Analysis or Test Options
Trace and Minor Elements				
Total	1,2,3	impinger(S07D)*	part/aerosol removal(S06) +acidic(P11), +acid digestion(P12)*	AA/ICP(A40)*
Volatile	1,2,3	impinger(S07D)*	acidic(P11)+ acid digestion(P12)*	AA/ICP(A40)*
Radioactivity				
Gross alpha, beta	2,3	impinger(S07D)*	acidic(P11)*	alpha, beta counting(A36)*
Organics				
Total Hydrocarbons	1,2,3,4,6	gas bomb* or bag(S13)	part/aerosol removal(S06) +H_2O removal(S04)*	GC-FID(A02)*
	5	screening(S08)*, or	NA	portable FID(S08)*
		bagging(S14)+gas bomb(S13)	NA	GC-FID(A02)
C_1-C_6 Hydrocarbons	2,3,4,6	gas bomb* or bag(S13)	part/aerosol removal(S06) +H_2O removal(S04)*	GC-FID(A02)*
Volatile Organics				
o Functional group screening	2,3,4,6	sorbent(S05)*	extraction(P01), or	spectrometric(A14)
			extraction(P01) + LC separation(P05)*, or	spectrometric(A14)*
			partitioning(P04)	spectrometric(A14)
o Aliphatics (C_1-C_{10})	2,3,4,6	gas bomb(S13)*, or	part/aerosol removal(S06) +H_2O removal(S04)*	GC-FID(A02)*
		sorbent(S05)	thermal desorption(P03)	GC/MS(A11), or GC-FID(A12)

(Continued)

TABLE 4-27. (continued)

Property or Specie	Generic Stream	Sampling Options	Preparation Options	Analysis or Test Options
o Aromatics				
- Simple(BTX)	2,3,4,6	gas bomb(S13), or	part/aerosol removal(S06) +H_2O removal(S04)	GC-FID(A02)
		sorbent(S05), or	extraction(P01),or partitioning(P04),	GC-FID(A02)+/or GC/MS(A11)+/or GC-FID(A12)+/or GC-PID(A19)
		sorbent(S05)*	thermal desorption(P03)*	GC-FID(A02)+/or GC/MS(A11)*+/or GC-FID(A12)+/or GC-PID(A19)*
- Polynuclear aromatics	2,3,4,6	sorbent(S05), or	extraction(P01) or	GC/MS(A11), GC-FID(A12), GC-PID(A19), HPLC(A16), GC/MS-SCM(A15)+/or
			extraction(P01) + LC separation (P05) or	GC/MS(A11), GD-FID(A12), GC-PID(A19), HPLC(A16), GC/MS-SCM(A15)+/or
			partitioning(P04)	GC/MS(A11), GD-FID(A12), GC-PID(A19), HPLC(A16), GC/MS-SCM(A15)+/or
		sorbent(S05)*	thermal desorption(P03)*	GC/MS(A11)*, GD-FID(A12), GC-PID(A19), HPLC(A16), GC/MS-SCM(A15)
o Nitrogenous Compounds				
- Nitrogen Hetero/Amines	2,3,4,6	sorbent(S05), or	extraction(P01), or	GC/MS(A11)+/or GC-FID(A12)+/or GC-NP/HECD-N(A10)
			extraction (P01) + LC separation (P05), or	GC/MS(A11)+/or GC-FID(A12)+/or GC-NP/HECD-N(A10)
			partitioning (P04)	GC/MS(A11)+/or GC-FID(A12)+/or GC-NP/HECD-N(A10)
		sorbent(S05)*	thermal desorption(P03)*	GC/MS(A11)*+/or GC-FID(A12)+/or GC-NP/HECD-N(A10)*
- Nitriles, Isocyanates	2,3,4,6	sorbent(S05), or	extraction(P01), or	GC/MS(A11)+/or GC-FID(A12)+/or GC-NP/HECD-N(A10)+/or HPLC(A16)
			extraction(P01)+derivitization(P02), or	GC/MS(A11)+/or GC-FID(A12) +/or GC-NP/HECD-N(A10)+/or HPLC(A16)
			partitioning(P04), or	GC/MS(A11)+/or GC-FID(A12)+/or GC-NP/HECD-N(A10)+/or HPLC(A16)

(Continued)

TABLE 4-27. (continued)

Property or Specie	Generic Stream	Sampling Options	Preparation Options	Analysis or Test Options
			partitioning(P04) and derivitization(P02), or	GC/MS(A11)+/or GC-FID(A12)+/or GC-NP/HECD-N(A10)+/or HPLC(A16)
			extraction(P01)+LC separation(P05), or	GC/MS(A11)+/orGC-FID(A12)+/or GC-NP/HECD-N(A10)+/or HPLC(A16)
			extraction(P01)+LC separatin(P05)+derivitization(P02)	GC/MS(A11)+/or GC-FID(A12)+/or GC-NP/HECD-N(A10)+/or HPLC(A16)
		sorbent(S05)*	thermal desorption(P03)*	GC/MS(A11)*+/or GC-FID(A12)+/or GC-NP/HECD-N(A10)*
o Oxygenates				
- Phenols	2,3,4,6	sorbent(S05), or	extraction(P01), or	GC/MS(A11)+/or C-FID(A12)+/or GC-PID(A19)+/or HPLC(A16)+/or GC/MS-SCM(A15)
			extraction(P01)+ LC separation(P05), or	GC/MS(A11)+/or GC-FID(A12)+/or GC-PID(A19)+/or HPLC(A16)+/or GC/MS-SCM(A15)
			extraction(P01)+ LC separation(P05)+ derivitization(P02), or	GC/MS(A11)+/or GC-FID(A12)+/or GC-PID(A19)+/or HPLC(A16)+/or GC/MS-SCM(A15)
			extraction(P01)+ derivitization(P02), or	GC/MS(A11)+/or GC-FID(A12)+/or GC-PID(A19)+/or HPLC(A16)+/or GC/MS-SCM(A15)
			partitioning(P04), or	GC/MS(A11)+/or GC-FID(A12)+/or GC-PID(A19)+/or HPLC(A16)+/or GC/MS-SCM(A15)
			partitioning(P04)+ derivitization(P02)	GC/MS(A11)+/or GC-FID(A12)+/or GC-PID(A19)+/or HPLC(A16)+/or GC/MS-SCM(A15)
		sorbent(S05)*	thermal desorption(P03)*	GC/MS(A11)*+/or GC-FID(A12)+/or GC-PID(A19)*+/or GC/MS-SCM(A15)

(Continued)

TABLE 4-27. (continued)

Property or Specie	Generic Stream	Sampling Options	Preparation Options	Analysis or Test Options
- Carboxylic Acids	2,3,4,6	sorbent(S05)	extraction(P01), or	GC/MS(A11)+/or GC-FID(A12)+/or HPLC(A16)
			extraction(P01)+ LC separation(P05), or	GC/MS(A11)+/or GC-FID(A12)+/or HPLC(A16)
			extraction(P01)+ LC separation(P05)+ derivitization(P02), or	GC/MS(A11)+/or GC-FID(A12)+/or HPLC(A16)
			extraction(P01)+ derivitization(P02), or	GC/MS(A11)+/or GC-FID(A12)+/or HPLC(A16)
			partitioning(P04), or	GC/MS(A11)+/or GC-FID(A12)+/or HPLC(A16)
			partitioning(P04)+ derivitization(P02)	GC/MS(A11)+/or GC-FID(A12)+/or HPLC(A16)
- Other	2,3,4,6	sorbent(S05),or	extraction(P01), or	GC/MS(A11)+/or GC-FID(A12)+/or HPLC(A16)
			extraction(P01)+ LC separation(P05), or	GC/MS(A11)+/or GC-FID(A12)+/or HPLC(A16)
			extraction(P01)+ LC separation(P05)+ derivitization(P02), or	GC/MS(A11)+/or GC-FID(A12)+/or HPLC(A16)
			extraction(P01)+ derivitization(P02), or	GC/MS(A11)+/or GC-FID(A12)+/or HPLC(A16)
			partitioning(P04), or	GC/MS(A11)+/or GC-FID(A12)+/or HPLC(A16)
			partitioning(P04)+ derivitization(P02)	GC/MS(A11)+/or GC-FID(A12)+/or HPLC(A16)
		sorbent(S05)*	thermal desorption(P03)*	GC/MS(A11)*+/or GC-FID(A12)+/or HPLC(A16)
o Sulfur Containing Compounds	2,3,4,6	sorbent(S05), or	extraction(P01), or	GC/MS(A11)+/or GC-FID(A12)+/or GC-FPD/HECD-S(A18)
			partitioning(P05), or	GC/MS(A11)+/or GC-FID(A12)+/or GC-FPD/HECD-S(A18)
			extraction(P01)+ LC separation(P05)	GC/MS(A11)+/or GC-FID(A12)+/or GC-FPD/HECD-S(A18)
		sorbent(S05)*	thermal desorption(P03)*	GC/MS(A11)*+/or GC-FID(A12)+/or GC-FPD/HECD-S(A18)*

(Continued)

TABLE 4-27. (continued)

Property or Specie	Generic Stream	Sampling Options	Preparation Options	Analysis or Test Options
Condensable Organics				
o Loading	2,3,4,6	sorbent(S05)*+/or impinger(S09)	cool(P11)+extraction (P01)*, or	GC-FID(A12)* +gravimetric(A13)*
			cool(P11)+extraction (P01)+LC separation (P05) or	GC-FID(A12) +gravimetric(A13)
			cool(P11)+partitioning (P04)	GC-FID(A12) +gravimetric(A13)
o Functional Group Screening	3,6	sorbent(S05)*+/or impinger(S09)	cool(P11)+extraction (P01), or	spectrometric(A14)
			cool(P11)+extraction (P01)+LC separation (P05)* or	spectrometric(A14)*
			cool(P11)+partitioning (P04)	spectrometric(A14)
o Aliphatics	2,3,4,6	sorbent(S05)*+/or impinger(S09)	cool(P11)+extraction (P01), or	GC/MS(A11)+/or GC-FID(A12)
			cool(P11)+extraction (P01)+LC separation (P05)+partitioning(P04)	GC/MS(A11)+/or GC-FID(A12)
			cool(P11)+partitioning (P04)	GC/MS(A11)+/or GC-FID(A12)
			cool(p11)+microextraction (P06)	GC/MS(A11)+/or GC-FID(A12)
o Aromatics				
- Simple (BTX)	2,3,4,6	sorbent(S05)*+/or impinger(S09)	cool(P11)+extraction (P01)*, or	GC/MS(A11)* +/or GC-FID(A12)+/or GC-PID(A19)* +/or HPLC(A16)+/or GC/MS-SCM(A15)
			cool(P11)+extraction (P01)+LC separation (P05)or	GC/MS(A11)+/or GC-FID(A12)+/or GC-PID(A19)+/or HPLC(A16)+/or GC/MS-SCM(A15)
			cool(P11)+partitioning (P04)	GC/MS(A11)+/or GC-FID(A12)+/or GC-PID(A19)+/or HPLC(A16)+/or GC/MS-SCM(A15)
- Polynuclear	2,3,4,6	sorbent(S05)*+/or impinger(S09)	cool(P11)+extraction (P01)*, or	GC/MS(A11)* +/or GC-FID(A12)+/or GC-PID(A19)* +/or HPLC(A16)+/or GC/MS-SCM(A15)
			cool(P11)+extraction (P01)+LC separation (P05)or	GC/MS(A11)+/or GC-FID(A12)+/or GC-PID(A19)+/or HPLC(A16)+/or GC/MS-SCM(A15)
			cool(P11)+partitioning (P04)	GC/MS(A11)+/or GC-FID(A12)+/or GC-PID(A19)+/or HPLC(A16)+/or GC/MS-SCM(A15)

(Continued)

TABLE 4-27. (continued)

Property or Specie	Generic Stream	Sampling Options	Preparation Options	Analysis or Test Options
o Nitrogenous Compounds				
- Nitrogen Hetero/Amines	2,3,4,6	sorbent(S05)*/or impinger(S09)	cool(P11)+extraction (P01)*, or	GC/MS(A11)*+/or GC-FID(A12)+/or GC-NP/HECD-N(A10)*
			cool(P11)+extraction (P01)+LC separation (P05)	GC/MS(A11)+/or GC-FID(A12)+/or GC-NP/HECD-N(A12)
			cool(P11)+partitioning (P04)	GC/MS(A11)+/or GC-FID(A12)+/or GC-NP/HECD-N(A12)
- Nitriles, Isocyanates	2,3,4,6	sorbent(S05)*+/or impinger(S09), or	cool(P11)+extraction (P01)*, or	GC/MS(A11)* +/or GC-FID(A12)+/or GC-NP/HECD-N(A10)* +/or HPLC(A16)
			cool(P11)+extraction (P01)+LC separation (P05), or	GC/MS(A11)+/or GC-FID(A12)+/or GC-NP/HECD-N(A10)+/or HPLC(A16)
			cool(P11)+extraction (P01)+derivitization (P02), or	GC/MS(A11)+/or GC-FID(A12)+/or GC-NP/HECD-N(A10)+/or HPLC(A16)
			cool(P11)+extraction (P01)+LC separation (P05)+derivitization (P02), or	GC/MS(A11)+/or GC-FID(A12)+/or GC-NP/HECD-N(A10)+/or HPLC(A16)
			cool(P11)+partitioning (P04), or	GC/MS(A11)+/or GC-FID(A12)+/or GC-NP/HECD-N(A10)+/or HPLC(A16)
			cool(P11)+microextraction(P06), or	GC/MS(A11)+/or GC-FID(A12)+/or GC-NP/HECD-N(A10)+/or HPLC(A16)
			cool(P11)+microextraction(P06),+derivitization (P02),	GC/MS(A11)+/or GC-FID(A12)+/or GC-NP/HECD-N(A10)+/or HPLC(A16)
		impinger(S09)	cool(P11)	aqueous inj.(A09)

(Continued)

TABLE 4-27. (continued)

Property or Specie	Generic Stream	Sampling Options	Preparation Options	Analysis or Test Options
o Oxygenates				
- Phenols	2,3,4,6	sorbent(S05)*+/or impinger(S09)	cool(P11)+extraction (P01)*, or	GC/MS(A11)*+/or GC-FID(A12)+/or GC-NP/HECD-N(A10)+/or HPLC(A16)+/or GC-PID(A19)
			cool(P11)+extraction (P01)+LC separation (P05), or	GC/MS(A11)+/or GC-FID(A12)+/or GC-NP/HECD-N(A10)+/or HPLC(A16)
			cool(P11)+extraction (P01)+derivitization (P02), or	GC/MS(A11)+/or GC-FID(A12)+/or GC-NP/HECD-N(A10)+/or HPLC(A16)
			cool(P11)+extraction (P01)+LC separation (P05)+derivitization (P02), or	GC/MS(A11)+/or GC-FID(A12)+/or GC-NP/HECD-N(A10)+/or HPLC(A16)
			cool(P11)+partitioning (P04), or	GC/MS(A11)+/or GC-FID(A12)+/or GC-NP/HECD-N(A10)+/or HPLC(A16)
			cool(P11)+microextraction(P06), or	GC/MS(A11)+/or GC-FID(A12)+/or GC-NP/HECD-N(A10)+/or HPLC(A16)
			cool(P11)+microextraction(P06),+derivitization (P02),	GC/MS(A11)+/or GC-FID(A12)+/or GC-NP/HECD-N(A10)+/or HPLC(A16)
- Carboxylic Acids	2,3,4,6	sorbent(S05)*+/or impinger(S09)	cool(P11)+extraction (P01), or	GC/MS(A11)+/or GC-FID(A12)+/or HPLC(A16)
			cool(P11)+extraction (P01)+LC separation (P05), or	GC/MS(A11)+/or GC-FID(A12)+/or HPLC(A16)
			cool(P11)+extraction (P01)+derivitization (P02)*, or	GC/MS(A11)*+/or GC-FID(A12)+/or HPLC(A16)
			cool(P11)+extraction (P01)+LC separation (P05)+derivitization (P02), or	GC/MS(A11)+/or GC-FID(A12)+/or HPLC(A16)

(Continued)

TABLE 4-27. (continued)

Property or Specie	Generic Stream	Sampling Options	Preparation Options	Analysis or Test Options
			cool(P11)+partitioning (P04), or	GC/MS(A11)+/or GC-FID(A12)+/or HPLC(A16)
			cool(P11)+microextraction(P06), or	GC/MS(A11)+/or GC-FID(A12)+/or HPLC(A16)
			cool(P11)+microextraction(P06),+derivitization (P02),	GC/MS(A11)+/or GC-FID(A12)+/or HPLC(A16)
		impinger(S09)	cool(P11)	aqueous inj.(A09)
- Others	2,3,4,6	sorbent(S05)*+/or impinger(S09)	cool(P11)+extraction (P01)*, or	GC/MS(A11)*+/or GC-FID(A12)+/or HPLC(A16)
			cool(P11)+extraction (P01)+LC separation (P05), or	GC/MS(A11)+/or GC-FID(A12)+/or HPLC(A16)
			cool(P11)+extraction (P01)+derivitization (P02), or	GC/MS(A11)+/or GC-FID(A12)+/or HPLC(A16)
			cool(P11)+extraction (P01)+LC separation (P05)+derivitization (P02), or	GC/MS(A11)+/or GC-FID(A12)+/or HPLC(A16)
			cool(P11)+partitioning (P04), or	GC/MS(A11)+/or GC-FID(A12)+/or HPLC(A16)
			cool(P11)+microextraction(P06), or	GC/MS(A11)+/or GC-FID(A12)+/or HPLC(A16)
			cool(P11)+microextraction(P06),+derivitization (P02),	GC/MS(A11)+/or GC-FID(A12)+/or HPLC(A16)
		impinger(S09)	cool(P11)	aqueous inj.(A09)
o Sulfur Containing Compounds	2,3,4,6	sorbent(S05)*+/or impinger(S09)	cool(P11)+extraction (P01)*, or	GC/MS(A11)*+/or GC-FID(A12)+/or GC-FPD/HECD-S(A18)*
			cool(P11)+extraction (P01)+LC separation (P05), or	GC/MS(A11)+/or GC-FID(A12)+/or GC-FPD/HECD-S(A18)
			cool(P11)+partitioning (P04), or	GC/MS(A11)+/or GC-FID(A12)+/or GC-FPD/HECD-S(A18)
			cool(P11)+microextraction(P06).	GC/MS(A11)+/or GC-FID(A12)+/or GC-FPD/HECD-S(A18)

TABLE 4-27. (continued)

FOOTNOTES:

Fractionation may be appropriate for complex organic samples. Fraction or fractions of interest can be selected prior to analysis. If capillary GC is implemented, fractionation (as indicated in Table 4-24) will be necessary less frequently.

GENERIC STREAMS:

1. Flue gases from conventional fuel combustion
2. Flue gases from process-derived fuel or waste combustion
3. Uncombusted vent gases or feed gases to flares
4. Tank vents
5. Process fugitive emissions
6. Impoundment, storage or disposal emissions
7. Fugitive particulate emissions

NA - not applicable

*Techniques expected to be most commonly applicable are marked with an asterisk

**See Table 4-29 for Solids Methods.

TABLE 4-28. MONITORING OPTIONS FOR AQUEOUS STREAMS

Property or Specie	Generic Stream	Sampling Options	Preparation Options	Analysis or Test Options
pH	1,2,3,4	grab(S11)*	NR	electrode(A20)*
Conductivity	1,2,3,4	grab(S11)*	cool(P11)*	electrode(T09)*
Alkalinity/Acidity	1,2,3,4	composite(S10)* or grab(S11)	cool(P11)*	titration(A39)*
Ammonia	1,2,3,4	composite(S10) or grab(S11)*	acidic + cool(P11)*	titration(A27)*
Cyanide	1,2,3,4	composite(S10) or grab(S11)*	basic + cool(P11)*	colorimetric(A28)*
Oil and Grease	1,3	composite(S10) or grab(S11)*	acidic + cool(P11)*	gravimetric(A37)*
Dissolved Oxygen	1,2,3,4	composite(S10)* or grab(S11)	cool(P11)*	electrode(A44)*
Chloride	1,2,3,4	composite(S10)* or grab(S11)	NR	titration(A33)*
Fluoride	1,2,3,4	composite(S10)* or grab(S11)	NR	SIE(A31)*
Nitrate/Nitrite	1,2,3,4	composite(S10) or grab(S11)*	acidic + cool(P11)*	colorimetric(A32)*
Sulfate	1,2,3,4	composite(S10)* or grab(S11)	cool(P11)*	turbitimetric(A35)*
Sulfite	1,2,3,4	composite(S10) or grab(S11)*	cool(P11)*	titration(A34)*
Sulfide	1,2,3,4	composite(S10) or grab(S11)*	filter(P11)*	titration(A29)*
Biological Oxygen Demand	1,2,3,4	composite(S10) or grab(S11)*	cool(P11)*	incubation(A25)*
Chemical Oxygen Demand	1,2,3,4	composite(S10) or grab(S11)*	acidic(P11)*	oxidation(A24)*
Phosphate	1,2,3,4	composite(S10) or grab(S11)*	phosphate forms separation(A38)*	colorimetric(A38)*
Thiocyanate	1,2,3,4	composite(S10) or grab(S11)*	cool(P11)*	colorimetric(A30)*
Formate	1,2,3,4	composite(S10) or grab(S11)*	cool(P11)*	ion chromatography (A45)*
Total Organic Carbon	1,3,4	composite(S10) or grab(S11)*	acidic + cool(P11)*	NDIR-FID(A42)*
Total Inorganic Carbon	1,2,3,4	composite(S10)* or grab(S11)	cool(P11)*	NDIR(A43)*
Trace and Minor Elements				
o Total	1,2,3,4	composite(S10)* or grab(S11)	acidic(P11) + acid digestion(P20)*	AA/ICP (A40)*
o Soluble	1,2,3,4	composite(S10)* or grab(S11)	filter + acidic(P11) + acid digestion(P20)*	AA/ICP (A40)*
Radioactivity	3,4	composite(S10)* or grab(S11)	acidic(P11)*	α,β counting (A36)*
Total Suspended Solids	1,2,3,4	composite(S10) or grab(S11)*	cool(P11)*	gravimetric (A23)*
Total Dissolved Solids	1,2,3,4	composite(S10) or grab(S11)*	cool(P11)*	gravimetric (A22)*
Total Solids	1,2,3,4	composite(S10) or grab(S11)*	cool(P11)*	gravimetric (A21)*
Total Volatile Solids	1,2,3,4	composite(S10) or grab(S11)*	cool(P11)*	gravimetric (A21)*

(Continued)

TABLE 4-28. (continued)

Property or Specie	Generic Stream	Sampling Options	Preparation Options	Analysis or Test Options
Settleable Solids	1,2,3,4	composite(S10) or grab(S11)*	cool(P11)*	sedimentation(A46)*
Solids Composition	3,4	composite(S10)* or grab(S11)	**	**
Organics				
o Loading	1,2,3,4	composite(S10) or grab(S11)*	cool(P11) + extraction(P01)*	gravimetric(A13) + GC-FID(A12)*
o Total Organic Halogens	3,4	composite(S10) or grab(S11)*	cool(P11)*	TOX(A17)*
o Functional Group Screening	1,3,4	composite(S10) or grab(S11)*	cool (P11) + extraction (P01), or cool (P11) + extraction (P01) + LC separation (P05)*, or cool (P11) + microextraction (P06), or cool (P11) + partitioning (P04)	spectrometric(A14) spectrometric(A14)* spectrometric(A14) spectrometric(A14)
o Phenolics	1,2,3,4	composite(S10) or grab(S11)*	acidic + cool(P11)*	colorimetric(A26)*
o Volatile Organics				
- Aliphatics	1,3,4	composite(S10) or grab(S11)*	cool(P11) + purge and trap (P03)*	GC/MS(A11)* +/or GC-FID(A12)
- Aromatics . Simple(BTX)	1,3,4	composite(S10) or grab(S11)*	cool(P11) + purge and trap (P03)*	GC/MS(A11)* +/or GC-FID(A12) +/or GC-PID(A19)*
. Polynuclear Aromatics	1,3,4	composite(S10) or grab(S11)*	cool(P11) + purge and trap(P03)*	GC/MS(A11)* +/or GC-FID(A12) +/or GC-PID(A19) +/or HPLC(A16) +/or GC/MS-SCM(A15)
- Nitrogenous Compounds				
. Nitrogen Hetero/ Amines	3,4	composite(S10) or grab(S11)*	cool(P11) + purge and trap(P03)*	GC/MS(A11)* +/or GC-FID(A12) +/or GC-NP/HECD-N*(A10)
. Nitriles, Isocyanates	3,4	composite(S10) or grab(S11)*	cool(P11) + purge and trap(P03)*	GC/MS(A11)* +/or GC-FID(A12) +/or GC-NP/HECD-N(A10)*
- Oxygenates				
. Phenols	3,4	composite(S10) or grab(S11)*	cool(P11) + purge and trap(P03)*	GC/MS(A11)* +/or GC-FID(A12) +/or GC-PID(A19)* +/or GC/MS-SCM(A15)
. Carboxylic Acids	3,4	composite(S10) or grab(S11)*	cool(P11) + purge and trap(P03)*	GC/MS(A11)* +/or GC-FID(A12) +/or GC-PID(A19) +/or HPLC(A16) +/or GC/MS-SCM(A15)
. Other	3,4	composite(S10) or grab(S11)*	cool(P11) + purge and trap(P03)*	GC/MS(A11)* +/or GC-FID(A12) GC/MS(A19) +/or GC/MS-SCM(A15)

(Continued)

TABLE 4-28. (continued)

Property or Specie	Generic Stream	Sampling Options	Preparation Options	Analysis or Test Options
- Sulfur Containing Compounds	3,4	composite(S10) or grab(S11)*	cool(P11) + purge and trap(P03)*	GC/MS(A11)* +/or GC-FID(A12) +/or GC-FPD/HECD-S(A18)*
o Nonvolatile Organics				
- Aliphatics	1,3,4	composite(S10)* or grab(S11)	cool (P11) + extraction (P01)*, or	GC/MS(A11)* +/or GC-FID(A12)
			cool (P11) + extraction (P01) + LC separation (P05), or	GC/MS(A11) +/or GC-FID(A12)
			cool (P11) + partitioning (P04), or	GC/MS(A11) +/or GC-FID(A12)
			cool (P11) + microextraction (P06)	GC/MS(A11) +/or GC-FID(A12)
- Aromatics				
. Simple(BTX)	1,3,4	composite(S10)* or grab(S11)	cool (P11) + extraction (P01)*, or	GC/MS(A11)* +/or GC-FID(A12) +/or GC-PID(A19)*
			cool (P11) + extraction (P01) + LC separation (P05), or	GC/MS(A11) +/or GC-FID(A12) +/or GC-PID(A19)
			cool (P11) + partitioning (P04), or	GC/MS(A11) +/or GC-FID(A12) +/or GC-PID(A19)
			cool (P11) + microextraction (P06)	GC/MS(A11) +/or GC-FID(A12) +/or GC-PID(A19)
. Polynuclear Aromatics	1,3,4	composite(S10)* or grab(S11)	cool (P11) + extraction (P01)*, or	GC/MS(A11)* +/or GC-FID(A12) +/or GC-PID(A19) +/or HPLC(A16)
			cool (P11) + extraction (P01) + LC separation (P05), or	GC/MS(A11) +/or GC-FID(A12) +/or GC-PID(A19) +/or HPLC(A16)
			cool (P11) + partitioning (P04), or	GC/MS(A11) +/or GC-FID(A12) +/or GC-PID(A19) +/or HPLC(A16)
			cool (P11) + microextraction (P06)	GC/MS(A11) +/or GC-FID(A12) +/or GC-PID(A19) +/or HPLC(A16)
- Nitrogeneous Compounds				
. Nitrogen Hetero/Amines	3,4	composite(S10)* or grab(S11)	cool (P11) + extraction (P01)*, or	GC/MS(A11)* +/or GC-FID(A12) +/or GC-NP/HECD-N(A10)* +/or HPLC(A16)
			cool (P11) + extraction (P01) + LC separation (P05), or	GC/MS(A11) +/or GC-FID(A12) +/or GC-NP/HECD-N(A10) +/or HPLC(A16)
			cool (P11) + partitioning (P04), or	GC/MS(A11) +/or GC-FID(A12) +/or GC-NP/HECD-N(A10) +/or HPLC(A16)
			cool (P11) + microextraction (P06)	GC/MS(A11) +/or GC-FID(A12) +/or GC-NP/HECD-N(A10) +/or HPLC(A16)

(Continued)

TABLE 4-28. (continued)

Property or Specie	Generic Stream	Sampling Options	Preparation Options	Analysis or Test Options
. Nitriles, Isocyanates	3,4	composite(S10)* or grab(S11)	cool (P11) + extraction (P01)*, or	GC/MS(A11)* +/or GC-FID(A12) +/or GC-NP/HECD-N(A10)* +/or HPLC(A16)
			cool (P11) + extraction (P01) + derivitization (P02), or	GC/MS(A11) +/or GC-FID(A12) +/or GC-NP/HECD-N(A10) +/or HPLC(A16)
			cool (P11) + extraction (P01) + LC separation (P05), or	GC/MS(A11) +/or GC-FID(A12) +/or GC-NP/HECD-N(A10) +/or HPLC(A16)
			cool (P11) + extraction (P01) + LC separation (P05) + derivitization (P02), or	GC/MS(A11) +/or GC-FID(A12) +/or GC-NP/HECD-N(A10) +/or HPLC(A16)
			cool (P11) + partitioning (P04), or	GC/MS(A11) +/or GC-FID(A12) +/or GC-NP/HECD-N(A10) +/or HPLC(A16)
			cool(P11) + microextraction(P06), or	GC/MS(A11) +/or GC-FID(A12) +/or GC-NP/HECD-N(A10) +/or HPLC(A16)
			cool (P11) + microextraction (P06) + derivitization (P02),or	GC/MS(A11) +/or GC-FID(A12) +/or GC-NP/HECD-N(A10) +/or HPLC(A16)
			cool(P11)	aqueous inj.(A09)
- Oxygenates				
. Phenols	3,4	composite(S10)* or grab(S11)	cool (P11) + extraction (P01)*, or	GC/MS(A11)* +/or GC-FID(A12) +/or GC-PID(A19)* +/or HPLC(A16) +/or GC/MS-SCM(A15)
			cool (P11) + extraction (P01) + derivitization (P02), or	GC/MS(A11) +/or GC-FID(A12) +/or GC-PID(A19) +/or HPLC(A16) +/or GC/MS-SCM(A15)
			cool (P11) + extraction (P01) + LC separation (P05), or	GC/MS(A11) +/or GC-FID(A12) +/or GC-PID(A19) +/or HPLC(A16) +/or GC/MS-SCM(A15)
			cool (P11) + extraction (P01) + LC separation (P05) + derivitization (P02), or	GC/MS(A11) +/or GC-FID(A12) +/or GC-PID(A19) +/or HPLC(A16) +/or GC/MS-SCM(A15)
			cool (P11) + partitioning (P04), or	GC/MS(A11) +/or GC-FID(A12) +/or GC-PID(A19) +/or HPLC(A16) +/or GC/MS-SCM(A15)
			cool (P11) + microextraction (P06), or	GC/MS(A11) +/or GC-FID(A12) +/or GC-PID(A19) +/or HPLC(A16) +/or GC/MS-SCM(A15)
			cool (P11) + microextraction (P06) + derivitization (P02)	GC/MS(A11) +/or GC-FID(A12) +/or GC-PID(A19) +/or HPLC(A16) +/or GC/MS-SCM(A15)

(Continued)

TABLE 4-28. (continued)

Property or Specie	Generic Stream	Sampling Options	Preparation Options	Analysis or Test Options
. Carboxylic Acids	3,4	composite(S10)* or grab(S11)	cool (P11) + extraction (P01)*, or	GC/MS(A11)* +/or GC-FID(A12) +/or HPLC(A16)*
			cool (P11) + extraction (P01) + derivitization (P02), or	GC/MS(A11) +/or GC-FID(A12) +/or HPLC(A16)
			cool (P11) + extraction (P01) + LC separation (P05), or	GC/MS(A11) +/or GC-FID(A12) +/or HPLC(A16)
			cool (P11) + extraction (P01) + LC separation (P05) + derivitization (P02), or	GC/MS(A11) +/or GC-FID(A12) +/or HPLC(A16)
			cool (P11) + partitioning (P04), or	GC/MS(A11) +/or GC-FID(A12) +/or HPLC(A16)
			cool (P11) + microextraction (P06), or	GC/MS(A11) +/or GC-FID(A12) +/or HPLC(A16)
			cool (P11) + microextraction (P06) + derivitization (P02),or	GC/MS(A11) +/or GC-FID(A12) +/or HPLC(A16)
			cool(P11)	aqueous inj.(A09)
. Other	3,4	composite(S10)* or grab(S11)	cool (P11) + extraction (P01)*, or	GC/MS(A11)* +/or GC-FID(A12) +/or HPLC(A16)
			cool (P11) + extraction (P01) + derivitization (P02), or	GC/MS(A11) +/or GC-FID(A12) +/or HPLC(A16)
			cool (P11) + extraction (P01) + LC separation (P05), or	GC/MS(A11) +/or GC-FID(A12) +/or HPLC(A16)
			cool (P11) + extraction (P01) + LC separation (P05) + derivitization (P02), or	GC/MS(A11) +/or GC-FID(A12) +/or HPLC(A16)
			cool (P11) + partitioning (P04), or	GC/MS(A11) +/or GC-FID(A12) +/or HPLC(A16)
			cool (P11) + microextraction (P06), or	GC/MS(A11) +/or GC-FID(A12) +/or HPLC(A16)
			cool (P11) + microextraction (P06) + derivitization (P02),or	GC/MS(A11) +/or GC-FID(A12) +/or HPLC(A16)
			cool(P11)	aqueous inj.(A09)

(Continued)

TABLE 4-28. (continued)

Property or Specie	Generic Stream	Sampling Options	Preparation Options	Analysis or Test Options
- Sulfur Containing Compounds	3,4	composite(S10)* or grab(S11)	cool(P11) + extraction(P01)*, or	GC/MS(A11)* +/or GC-FID(A-12) +/or GC-FPD/HECD-S(A18)*
			cool(P11) + partitioning(P04), or	GC/MS(A11) +/or GC-FID(A-12) +/or GC-FPD/HECD-S(A18)
			cool(P11) + extraction(P01) + LC separation(P05), or	GC/MS(A11) +/or GC-FID(A-12) +/or GC-FPD/HECD-S(A18)
			cool(P11) + microextraction(P06)	GC/MS(A11) +/or GC-FID(A-12) +/or GC-FPD/HECD-S(A18)
Bioassay				
Health Effects	3,4	composite(S10)* or grab(S11)	cool(P11)*	cellular, mammalian (T12)*
Ecological Effects	3,4	composite(S10)* or grab(S11)	cool(P11)*	algal, vertebrate(T13)*

FOOTNOTES:

Fractionation may be appropriate for complex organic samples. Fraction or fractions of interest can be selected prior to analysis. If capillary GC is implemented, fractionation (as indicated in Table 4-25) will be necessary less frequently.

Generic Stream Types
1. Wastewater streams containing nonunique streams from organic sources
2. Wastewater streams containing nonunique streams from organic-free or organic-lean sources
3. Wastewater streams containing unique streams from organic-laden sources
4. Wastewater streams containing unique streams from organic-free or organic-lean sources

*Expected to be most commonly applicable.

**See Table 4-29, MONITORING OPTIONS FOR SOLID STREAMS

NR - none required

TABLE 4-29. MONITORING OPTIONS FOR SOLID STREAMS

Property or Specie	Generic Stream	Sampling Options	Preparation Options	Analysis or Test Options
Proximate	1,2,3,4	composite* or grab (S01)	NR	ASTM(A04)*
Ultimate	1,2,3,4	composite* or grab (S01)	NR	ASTM(A05)*
Ash Mineral Analysis	1,2,3,4	composite* or grab (S01)	fusion(P09)* +/or acid digestion(P10)*	AA/ICP(A40)*
Trace and Minor Elements	1,2,3,4	composite* or grab (S01)	fusion(P09)* +/or acid digestion(P10)*	AA/ICP(A40)*
ASTM Leachability	1,2,3,4	composite* or grab (S01)	neutral extraction(P08)*	**
RCRA EP Leachability	1,2,3,4	composite* or grab (S01)	acid extraction(P07)*	**
Crystalline forms	3,4	composite* or grab (S01)	grind(A07)*	XRD(A07)*
Particle Size	1,2,3,4	composite* or grab (S01)	NR	SEM(A08)* or sieve and sedimentation(T05)
Surface Area	3,4	composite* or grab (S01)	dry(T11)*	BET(T11)*
Particle Morphology	3,4	composite* or grab (S01)	NR	SEM(A08)*
Reactivity	1,2,3,4	composite* or grab (S01)	NR	reaction with H_2O (T02)*
Ignitability	1,2,3,4	composite* or grab (S01)	NR	Pensky-Martens cup (T03)*
Corrosivity	1,2,3,4	composite* or grab (S01)	filter (T01)	steel coupon(T01)*
Radioactivity	1,2,3,4	composite* or grab (S01)	slurry or digestion (A06)	α, β, Ra226 counting (A06)*
Viscosity	1,2,3,4	composite* or grab (S01)	NR	viscometer(T10)*
Specific Gravity	1,2,3,4	composite* or grab (S01)	dry(T06)	displacement(T06)*
Bulk Density	2,4	composite* or grab (S01)	NR	densitometer(T07)*
Permeability	2,4	composite* or grab (S01)	NR	H_2O conductivity(T04)*
Organics***				
• Loading	1,3,4	composite* or grab (S01)	extraction(P01)	gravimetric(A13)+ GC-FID(A12)*
• Functional Group Screening	1,3,4	composite* or grab (S01)	extraction(P01), or extraction(P01) + LC separation(P05)*	spectrometric(A14) spectrometric(A14)*
• Aliphatics	1,3,4	composite* or grab (S01)	extraction(P01)*, or extraction(P01) + LC separation(P05)	GC/MS(A11)* +/or GC-FID(A12) GC/MS(A11) +/or GC-FID(A12)
• Aromatics				
- Simple(BTX)	1,3,4	composite* or grab (S01)	extraction(P01)*, or extraction(P01) + LC separation(P05)	GC/MS(A11)* +/or GC-FID(A12) +/or GC-PID(A19)* GC/MS(A11) +/or GC-FID(A12) +/or GC-PID(A19)*
- Polynuclear Aromatics	1,3,4	composite* or grab (S01)	extraction(P01)*, or extraction(P01) + LC separation(P05)	GC/MS(A11)* +/or GC-FID(A12) +/or GC-PID(A19) +/or HPLC(A16) +/or GC/MS-SCM(A15) GC/MS(A11) +/or GC-FID(A12) +/or GC-PID(A19) +/or HPLC(A16) +/or GC/MS-SCM(A15)

(Continued)

TABLE 4-29. (continued)

Property or Specie	Generic Stream	Sampling Options	Preparation Options	Analysis or Test Options
• Nitrogenous Compounds				
- Nitrogen Hetero/ Amines	3,4	composite* or grab(S01)	extraction(P01)*, or	GC/MS(A11)* +/or GC-FID(A12) +/or GC-NP/HECD-N(A10)* +/or HPLC(A16)
			extraction(P01) + LC separation(P05), or	GC/MS(A11) +/or GC-FID(A12) +/or GC-NP/HECD-N(A10) +/or HPLC(A16)
			extraction(P01) + derivitization(P02),or	GC/MS(A11) +/or GC-FID(A12) +/or GC-NP/HECD-N(A10) +/or HPLC(A16)
			extraction(P01) + LC separation(P05) + derivitization(P02)	GC/MS(A11) +/or GC-FID(A12) +/or GC-NP/HECD-N(A10) +/or HPLC(A16)
- Nitriles, Isocyanates	3,4	composite* or grab(S01)	extraction(P01)*, or	GC/MS(A11)* +/or GC-FID(A12) +/or GC-NP/HECD-N(A10)* +/or HPLC(A16)
			extraction(P01) + LC separation(P05),	GC/MS(A11) +/or GC-FID(A12) +/or GC-NP/HECD-N(A10) +/or HPLC(A16)
			extraction(P01) + derivitization(P02),or	GC/MS(A11) +/or GC-FID(A12) +/or GC-NP/HECD-N(A10) +/or HPLC(A16)
			extraction(P01) + LC separation(P05) + derivitization(P02)	GC/MS(A11) +/or GC-FID(A12) +/or GC-NP/HECD-N(A10) +/or HPLC(A16)
• Oxygenates				
- Phenols	3,4	composite* or grab(S01)	extraction(P01)*, or	GC/MS(A11)* +/or GC-FID(A12) +/or GC-PID(A19)* +/or HPLC(A16) +/or GC/MS-SCM(A15)
			extraction(P01) + LC separation(P05),	GC/MS(A11) +/or GC-FID(A12) +/or GC-PID(A19) +/or HPLC(A16) +/or GC/MS-SCM(A15)
			extraction(P01) + derivitization(P02),or	GC/MS(A11) +/or GC-FID(A12) +/or GC-PID(A19) +/or HPLC(A16) +/or GC/MS-SCM(A15)
			extraction(P01) + LC separation(P05) + derivitization(P02)	GC/MS(A11) +/or GC-FID(A12) +/or GC-PID(A19) +/or HPLC(A16) +/or GC/MS-SCM(A15)

(Continued)

TABLE 4-29. (continued)

Property or Specie	Generic Stream	Sampling Options	Preparation Options	Analysis or Test Options
- Carboxylic Acids	3,4	composite* or grab(S01)	extraction(P01)*, or	GC/MS(A11)* +/or GC-FID(A12) +/or HPLC(A16)* +/or GC-PID (A19)
			extraction(P01) + LC separation(P05),	GC/MS(A11) +/or GC-FID(A12) +/or HPLC(A16) +/or GC-PID (A19)
			extraction(P01) + derivitization(P02),or	GC/MS(A11) +/or GC-FID(A12) +/or HPLC(A16) +/or GC-PID (A19)
			extraction(P01) + LC separation(P05) + derivitization(P02)	GC/MS(A11) +/or GC-FID(A12) +/or HPLC(A16) +/or GC-PID (A19)
- Other	3,4	composite* or grab(S01)	extraction(P01)*, or	GC/MS(A11)* +/or GC-FID(A12) +/or HPLC(A16) +/or GC-PID (A19)
			extraction(P01) + LC separation(P05),	GC/MS(A11) +/or GC-FID(A12) +/or HPLC(A16) +/or GC-PID (A19)
			extraction(P01) + derivitization(P02),or	GC/MS(A11) +/or GC-FID(A12) +/or HPLC(A16) +/or GC/PID (A19)
			extraction(P01) + LC separation(P05) + derivitization(P02)	GC/MS(A11) +/or GC-FID(A12) +/or HPLC(A16) +/or GC-PID (A19)
o Sulfur Containing	3,4	composite* or grab(S01)	extraction(P01)*, or	GC/MS(A11)* +/or GC-FID(A12) +/or GC-FPD/HECD-S(A18)*
			extraction(P01) + LC separation (P05)	GC/MS(A11) +/or GC-FID(A12) +/or GC-FPD/HECD-S(A18)
Bioassay				
Health Effects	3,4	composite* or grab(S01)	NR	cellular,mammalian (T12)
		composite* or grab(S01)	neutral extraction (P08)*	cellular,mammalian (T12)*
Ecological Effects	3,4	composite* or grab(S01)	NR	algal, vertebrate(T13)
		composite* or grab (S01)	neutral extraction (P08)*	algal, vertebrate(T13)*

FOOTNOTES:

Fractionation may be appropriate for complex organic samples. Fraction or fractions of interest can be selected prior to analysis. If capillary GC is implemented, fractionation (as indicated in Table 4-26) will be necessary less frequently.

Generic Stream Types
1. Nonunique organic-laden solid wastes
2. Nonunique organic-free or organic-lean solid wastes
3. Unique organic-laden solid wastes
4. Unique organic-free or organic-lean solid wastes

*Expected to be most commonly applicable.

**See Table 4-28 MONITORING OPTIONS FOR AQUEOUS STREAMS

***Purging or thermal desorption techniques (P03), which define volatile organic fractions for liquids and gases, are not generally appropriate for solids. Therefore, no volatile organic classification is shown for solids.

NR - none required

4.5 REFERENCES FOR SECTION 4

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SECTION 5

AMBIENT MONITORING

Ambient monitoring is a key link defining the relationship between emissions from synthetic fuels production and impacts on human health and the environment. Ambient monitoring identifies potential contaminants in the environment, in the vicinity of the potential receptor, so that transport and potential degree of exposure to emissions can be estimated. Ambient monitoring includes chemical analyses and biological studies (genotoxic, mutagenic, and aquatic and terrestrial effects) on samples obtained from the environment in the vicinity of a synfuel facility. The biological component of the ambient program should provide help in identifying effects associated with plant discharges. The media which act as pathways for pollutant movement and which require monitoring include water within soil (i.e., vadose or unsaturated zone), surface aquifers, deep aquifers, surface waters, and the atmosphere. Ambient monitoring, as considered here, also includes monitoring of the soil itself.

While a large body of literature exists on the subject of ambient monitoring, certain references are of particular importance. Key references dealing with groundwater and the unsaturated zone are: 5-1, 5-2, 5-3 and 5-4; for the analyses of organic compounds: 5-5, 5-6, 5-7, 5-8, 5-9 and 5-10; for bioaccumulation: 5-11 and 5-12; for genotoxins: 5-13, 5-14, 5-15, 5-16, and 5-17; for analysis of complex mixtures: 5-18; and for an overall approach to monitoring a synthetic fuel facility: 5-19 and 5-20.

This section on ambient monitoring has a format similar to Section 4 for source monitoring. Section 5.1 describes suggested total data base needs to consider in designing the ambient portion of a monitoring plan or outline (analogous to Section 4.1), including substances of potential interest for monitoring and criteria for selecting locations for ambient monitoring stations. Section 5.2 describes approaches for conducting the ambient monitoring program (including the concept of phasing and discussions of the timing and frequency of monitoring), analogous to Sections 4.2 and 4.3. Section 5.3 addresses possible alternative ambient sampling and analytical techniques, analogous to Section 4.4. Section 5.4 discusses regional considerations in selecting aspects to be emphasized in ambient monitoring. Section 5.5 contains references for the whole section. While source monitoring occurs only during plant operation, ambient monitoring also includes the pre-construction and construction periods.

5.1 AMBIENT MONITORING DATA BASE SUGGESTIONS

5.1.1 Monitoring Suggestions to Define the Data Base

Oil shale, coal and tar sands, the basic resources for synthetic fuels plants, are of sedimentary origin. They are largely organic substances rich in heterocyclic nitrogen, oxygen, and sulfur compounds; polycyclic aromatic compounds; and inorganic mineral impurities. The oil shale, coal or tar sands processed at a specific site will contain varying amounts of complex organometallic materials depending on the meteorological, biological, and physical forces affecting bed formation. Consequently, each synfuel facility will have its own chemical "signature" depending on the ratios of these resource constituents and the manner in which they are converted into organic and inorganic pollutants in various solid, aqueous and airborne emissions.

In view of the wide array of potential site-specific emissions, the monitoring suggestions in Section 4.1.2 for the source discharge data base include the following elements:

- survey analytical techniques--well-defined screening procedures for a variety of substances. The survey approach avoids the need to judge, *a priori*, which specific substances might be discharged to the ambient environment from a specific synfuels plant.
- specific component analyses--analyses for individual substances (or properties, such as BOD) of regulatory or other interest.

- biological tests

In selecting the scope of the data base for ambient monitoring around a facility, the monitoring plan designer should:

- pay close attention to plans for the source monitoring data base (survey techniques, specific component analyses, bioassays); and
- consider the groupings of chemicals defined in Appendix C and specific biological tests (Appendices D and H) which are of particular concern for evaluating possible impacts on human health and the environment.

The survey techniques, specific component analyses and bio-assays suggested for source monitoring are summarized in Tables 4-4 through 4-6 (supplemented by Tables 4-7 through 4-9). A list of some specific substances likely to be detected in source surveys is included in Tables 4-10 and 4-11. The needs of the ambient monitoring program might vary from these source tables in some cases due to applicability of techniques and transformation/dilution of substances in the ambient environment. However, much of the information can be useful in the ambient program design, and use of the tables should provide a basis for correlating the results of source and ambient monitoring.

The ambient monitoring effort may have different emphasis from the source effort. For example, differences might arise due to chemical transformation in the environment, dilution of the substances through dispersion, and media effects (e.g., substances emitted in gaseous form might appear/accumulate in surface waters or soil). Accordingly, in addition to the substances listed in the source monitoring tables, the ambient monitoring effort should consider the groups of chemicals described in Appendix C. Most of these chemicals should, if present, be detected by the survey techniques mentioned previously, as well as those listed in Appendices D, E, and F. In addition to the acute bioassays listed in Table 4-9, the ambient program might also address the extended, ambient bioassays described in Appendix H (including terrestrial effects, periphyton, and aquatic bioaccumulation monitoring).

As noted above, the source monitoring techniques presented in Tables 4-4 through 4-6, in Section 4.4, and in Appendix A will be applicable to most substances or classes of compounds of interest in ambient monitoring. In particular, the methods of analysis will be applicable to samples collected in both the source and ambient monitoring programs (criteria pollutants in ambient air are an exception; special requirements are described in Appendix D).

Different sample collection and preparative methods, however, will be required for the ambient monitoring program. The concentrations of substances of interest generally will be much lower in ambient media than in source discharge streams. Therefore, larger sample volumes, longer sample collection periods, and techniques for concentrating samples to bring analytes into the detectable range will be required for ambient samples. Methods of sample collection and analysis for ambient air, surface water, soil and groundwater are discussed in detail in Appendices D, E, F, and G.

5.1.2 Location of Ambient Sampling Sites

A key element in developing the ambient data base is placement of sampling stations. Monitors should be sited so that any substances from the synfuels plant that affect the environment are detected, and so that the impacts of the plant can be distinguished from those of neighboring facilities.

In addition to obvious considerations such as accessibility, availability of electrical power, and relationship to possible interfering pollutant sources, important factors in selecting sampling sites are meteorology and topography. Dispersion modeling, if required to support PSD permit applications, will provide site-specific predictions of emission transport patterns that will be useful in siting air monitoring stations. The unidirectional movement of rivers and most groundwaters will, to a large extent, limit choices in placement of water samplers. However, both air and water monitoring will require site-specific strategies that provide both background (upstream, upwind) data and impact (downstream, downwind) data on the contribution from the synfuels plant. The approach to monitoring controlled emissions is well established and a detailed discussion is beyond the scope of this brief document. Detailed information can be found in references 5-21 through 5-32.

It is important that air monitoring stations provide data that are representative of background conditions (upwind of plant) and impact conditions (downwind of plant). If a wind rose pattern indicates that wind direction variations are seasonal, a number of stations may be needed around the perimeter of the facility. If a downwind impact station regularly samples emissions from other local sources, relocations should be considered. Meterological data should be collected to provide a basis for data interpretation.

5.2 APPROACHES FOR AMBIENT MONITORING

5.2.1 Pre-construction Monitoring

Pre-construction monitoring should be conducted to characterize the nature and extent of existing substances in the air, water, and soil in the vicinity of a proposed synfuel facility. Knowledge of these background concentrations is needed to assess the impact of the proposed source. Baseline meteorological and hydrological conditions should be monitored in addition to the substances expected to be emitted from the facility. Sampling sites should be located at the points of maximum expected concentrations due to emissions from the proposed facility, from existing sources, or the combined effects of both.

It would be desirable in most cases to conduct pre-construction monitoring for the pertinent portions of the entire suggested (chemical and biological) data base, as described in Section 5.1.1. The frequency and duration of pre-construction monitoring would depend upon the capabilities and costs of available ambient monitoring techniques (discussed in Appendices D through H), and on expected seasonal variations in meteorology and hydrology. The selected frequency also would depend on the precision of the ambient measurements and the desired statistical accuracy of the pre-construction results. The statistical considerations in selecting source monitoring frequency and duration discussed in Section 4.2.1.2 should also apply to ambient monitoring.

It is important that pre-construction monitoring begin early enough and last long enough (preferably at least one year) to collect data that are representative of normal seasonal changes. If a longer pre-construction monitoring period is possible and if additional accuracy in results is desirable, the duration might be lengthened as discussed in Section 4.2.1.2 for source monitoring. High priority should be placed on preparing and implementing the pre-construction portion of the monitoring plan, so it can be underway while detailed plant design and other pre-construction planning efforts proceed.

5.2.2 Construction Monitoring

Although the period of construction of a synfuel facility is brief compared to its operational life, it is during construction that the most dramatic alterations to the site, and on occasion to adjacent areas, will occur. Such large-scale activities, which are by nature relatively uncontrolled, require careful and continuous monitoring to assess the impact on the surrounding environment.

Construction monitoring is conducted from the initial phases of site preparation through completion of facility construction. It is essentially a continuation of the baseline monitoring initiated in the pre-construction phase. Its main function is to detect changes in environmental conditions that may be attributable to construction activities in order to minimize adverse impacts. Data acquired during construction will not only aid in the identification of impacts associated with construction activities *per se*, but also will expand the base of available background data collected in pre-construction monitoring. While construction monitoring requirements generally will be defined by the permitting process, they also should be addressed specifically in the monitoring outline and plan.

Ambient impacts from the construction of synfuels plants will be very similar to impacts from the construction of fossil fuel processing plants, and the same is true for the associated construction monitoring. Typical construction activities such as blasting, excavation, hauling, clearing and burning of vegetation, open pit dumping, and stock-piling of sand, gravel and other materials on site can result in excessive particulate emissions. In general, emissions of gaseous pollutants will not be significant during the construction phase. However, the use of diesel engines in both construction machinery and electrical generators will contribute to increased emissions of NO_x, CO and unburned hydrocarbons. If pre-construction monitoring indicates that levels of these pollutants are approaching National or state air quality standards, monitoring downwind of the site should be planned.

As noted in 5.1.1, the organic resources used as raw materials for synthetic fuel processes can be rich in sulfur, nitrogen, and organo-metallic compounds. In the event these compounds are exposed to the atmosphere, either through test burns (e.g., during in-situ retort construction) or as waste materials removed from the site, appropriate monitoring should be done. Such monitoring should be designed to account for the specific emission expected from construction or pre-operational activities. For example, sulfur dioxide and particulate monitoring would be performed when combustion trials occur, and elemental analyses of particulate samples and ambient NMHC measuremets would be done if mine waste or other residual organic materials were allowed to accumulate on site.

The schedule and duration of ambient air monitoring should correspond to the character of the activities at the construction site. At a minimum, upwind-downwind particulate sampling sites should be established and operated on an every-six-day schedule. If significant NO_2 levels have been measured during pre-construction monitoring, a downwind continuous NO_2 monitoring program should also be considered. Early in the construction phase, special purpose upwind-downwind property line studies would be useful in determining the impact of specific particulate sources such as loading facilities, truck traffic on access roads, and excavation and blasting. Finally, special activities at the site (e.g., disposal of waste materials by burning), should be monitored by the appropriate method at the time of occurrence.

Anticipated impacts to the soil and surface/ground-water systems from synfuels facility construction are also similar to those expected in conventional plant construction. Necessary modifications to the existing topography associated with site preparation, road and pipeline construction, etc., could result in impacts on runoff, erosion, and sedimentation rates. Accidental spills of oil, grease, or other materials on-site during construction activities could result in environmental contamination. Other potential sources of construction phase contaminants include wastewater from sanitary facilities and mine dewatering (where applicable), and landfill of construction waste.

Potential impacts specific to synfuels production are due to the nature of the raw materials and the modes of extraction peculiar to the industry. The extremely large volumes of material involved in either surface retorting or in-situ gasification of oil shale present a unique set of potential environmental problems. Stockpiled raw materials (surface-mined coal or lignite, oil shale, etc.) and/or overburden removed during mine construction could potentially generate acid, alkaline or trace element contaminated runoff or leachate. In-situ extraction technologies requiring fracturing of source materials prior to gasification could contribute to deterioration of groundwater quality if resulting fractures hydraulically connect shallow potable and deeper saline aquifers. Thus, the construction monitoring program might include:

- stream gaging - to identify variations in surface water flow beyond expected seasonal/episodic fluctuations;
- surface water quality monitoring - including chemical analysis, turbidity, and sedimentation rate determinations;

- ground-water monitoring - including sampling and water quality analysis and water table measurement;
- soil sampling and analysis - especially in the vicinity of known spills;
- runoff from overburden - special emphasis should be placed on the analysis of soluble metals (e.g., Se, As, Mo) under the alkaline runoff conditions potentially present in western soils.

5.2.3 Operational Monitoring

It is suggested that ambient monitoring conducted during plant operation employ a phased monitoring approach. A phased approach offers the opportunity to tailor the monitoring program to the specific site, providing extended coverage of a fairly extensive data base while reducing the extent and cost of the monitoring program. One concept for a phased source monitoring program is discussed in detail in Section 4.2; some alternatives (including an alternative involving no phasing) are addressed in Section 4.3. These concepts should apply to the ambient monitoring program as well.

5.2.3.1 Phase 1 Monitoring

When a synthetic fuels plant has achieved normal operation, the comprehensive Phase 1 ambient monitoring program might logically begin. In Phase 1, samples from all media (vadose zone, surface aquifers, deep aquifers, surface waters, the atmosphere and the soil) are surveyed for the pertinent portions of the total data base. As described in Section 5.1.1, this data base includes the application of survey analytical techniques, specific component analyses and biological testing. The Phase 1 design would include tests applicable to each medium. Permit-required monitoring would be superimposed on this survey monitoring.

The focus of this phase would be to identify those substances actually present in the ambient environment as a result of plant operation. The results of this Phase 1 program would be used for two purposes:

- to compare the results to the pre-construction monitoring data base, to develop initial conclusions regarding the environmental impact of the synfuels plant;
- to design a reduced Phase 2 operational monitoring program, as discussed in Section 5.2.3.2.

The frequency with which the various monitoring techniques (survey analytical techniques, specific component analyses, and biological tests) are conducted during Phase 1 depends on both practical and statistical considerations. From a practical standpoint, the frequency will be influenced by the capabilities and the costs of the applicable ambient monitoring techniques, described in Appendices D through H. From a statistical standpoint, the frequency (and the duration) of Phase 1 will be influenced by desired accuracy of the results, the variability in concentrations of the substances being monitored, and variations in hydrologic and meterologic conditions at the site. The suitable frequency might vary from substance to substance. Statistical considerations in selecting monitoring frequency and duration for source monitoring discussed in Section 4.2.1.2 should be applicable to ambient monitoring as well.

Phase 1 monitoring would continue for some limited period after routine plant operation begins. The duration of Phase 1 could be selected based on practical and statistical considerations and should include major seasonal variations in meteorological and hydrological conditions. A reasonable minimum duration will probably be about one year for most substances in most media, but a longer period might be required for groundwater monitoring, depending on pollutant migration rates.

Initial operation of a synfuels plant will generally involve a phased startup period. During startup plant discharges will not be representative of routine operation. In particular, excursions in the compositions of plant discharges are likely to occur; hence the startup period would not generally be suitable for Phase 1 (data base development) monitoring. Monitoring during the startup period can be used to validate ambient sampling and analytical procedures and to train monitoring personnel in preparation for formal Phase 1 monitoring. These startup results can also be used to gain an understanding of the substances present in the ambient environment due to plant operation, and to test the relationships between data collected by source and ambient monitoring. Compliance monitoring required by permits would proceed as scheduled during the startup period.

Possible methods of designing a startup source monitoring effort that will achieve appropriate quality assurance/protocol validation objectives are discussed in Section 4.2.1.3.

5.2.3.2 Phase 2 Monitoring

The intent of Phase 2 is to provide extended-term tracking of the Phase 1 data base, through a monitoring effort that is reduced in comparison with the Phase 1 program. The Phase 2 program should provide a data base reflecting a range of plant cycles/operating conditions. It should also provide a sufficient data history to enable reliable extrapolation of the data base to future facilities.

Three alternative approaches are discussed in Sections 4.2 and 4.3 for design of Phase 2 of the source monitoring program. The same approach can be applied to ambient monitoring.

- Use the Phase 1 results to select a limited number of "indicator" parameters to represent the data observed during Phase 1. Phase 2 monitoring would then address only those indicators. Portions of Phase 1 would be repeated if an excursion in an indicator suggests that the represented substances might also have varied.

- Use the Phase 1 results to decide which of the substances/parameters observed in Phase 1 should continue to be monitored; discontinue monitoring for the other substances, unless subsequent data suggest that monitoring for these (or additional) substances should be resumed.

- Continue the full Phase 1 program for some period (several years), without attempting to design a reduced Phase 2 program.

The first alternative approach above involves several decisions:

- What criteria can be used to determine when one substance/parameter might serve as a Phase 2 indicator for others? Suggestions concerning this issue are presented in Section 4.2.2.1 (including a discussion of statistical considerations, and including Table 4-20, which suggests certain substances that might be investigated as potential indicators). Where substances of particular interest in the ambient monitoring program (Appendix C) are not specifically listed in Table 4-20, potential indicators might be selected for these substances based on the results of Phase 1 monitoring and chemical and engineering judgment.
- How frequently should Phase 2 monitoring be conducted? This issue is decided based on practical and statistical considerations, as discussed in Section 4.2.2.2 as well as variations in meteorological and hydrological conditions.
- How should Phase 1 and Phase 2 results be compared, and how large an excursion might be permitted in the Phase 2 indicator before Phase 1 is repeated for the substances represented by that indicator? Statistical considerations for addressing this issue are discussed in Section 4.2.2.2.

With the Phase 2 indicator approach, the Phase 1 data base would be updated on a number of occasions, as discussed in Section 4.2.2.3.

The preceding discussion concerning phased approaches applies primarily to monitoring for chemical substances/parameters and to some short-term bio-assays. By comparison, some of the biological tests (such as the aquatic bio-accumulation test) might be inherently long-term, and hence not amenable to the type of phasing envisioned here.

5.3 ALTERNATIVE AMBIENT MONITORING PROCEDURES

A wide variety of alternative sampling and analytical procedures can be considered for the development of the data base described in Section 5.1.1, in all of the media of interest (vadose zone, surface aquifers, deep aquifers, surface waters, the atmosphere and the soil). Alternative procedures are described in Appendices D (air monitoring), E (water monitoring) and F (soil monitoring). Appendix G discusses some techniques for groundwater monitoring (of special concern for in-situ synfuels processes and some solid waste disposal operations).

Screening procedures for the determination of organic compounds in air and water, including sample collection, extraction, purification, and analysis are provided in Appendices D, E, and F.

Biological tests for the presence of airborne genotoxic and mutagenic agents are discussed in Appendix D. Special terrestrial and aquatic monitoring techniques which are suggested for incorporation into an ambient monitoring plan are described in Appendix H.

5.4 SPECIAL REGIONAL CONSIDERATIONS

Although it is important to survey the environment near synthetic fuels facilities for all groups of compounds of concern, certain pollutants or monitoring needs are likely to warrant special regional attention. Such variations in regional emphasis need to be considered in each monitoring plan and in any trend toward standardization of monitoring plans for all U.S. synfuels facilities. A few of these regional concerns are highlighted in this section. They should be viewed as examples of inherent variations in the relative importance of certain substances or characteristics from a geographical perspective.

5.4.1 Acidity/Alkalinity

The oxidation and dissolution of pyrite with the liberation of acid is responsible for the acid mine drainage problems which are a concern associated with the development of coal resources in the eastern United States. In the West, excessive amounts of alkaline calcite and dolomite in overburden material, coupled with sulfides, result in high total dissolved solid concentrations in surface waters and groundwaters. While decreasing the mobility of most metal species by increasing pH values, this process enhances the transport of other potential contaminants such as molybdenum, fluoride, boron, arsenic, selenium, and sulfate. These elements and their compounds may pose long-term detrimental environmental effects associated with chronic leaching of alkaline spoils (5-33, 5-34).

5.4.2 Sulfur and Trace Elements

Western lignites and subbituminous coals are low in sulfur content (usually less than 0.5 percent by weight), whereas the bituminous formations in the midwest may contain up to eight times as much sulfur (as high as 4.0 percent by weight, Reference 5-35). This disparity in sulfur levels can have a direct bearing on the magnitude of both water discharges and airborne emissions of inorganic and organic sulfur compounds.

Generally, coals in western states contain lower concentrations of environmentally objectionable trace elements than do the coals of eastern or midwestern states. However, the highest concentrations of arsenic, antimony, beryllium, cadmium, and selenium generally occur in coals from western states, and lead, mercury, and zinc are highest in eastern states. Appalachian coals also can be unusually high in beryllium, whereas the Powder River Basin coals of southeastern Montana and northwestern Wyoming are unusually low in most environmentally hazardous trace elements (5-36). For a current comprehensive review of trace elements of health and environmental concern in U.S. coals, see Reference 5-37.

5.4.3 Radioactive Materials

Radioactive isotopes can be found in coals of all ranks and are more prevalent in some lignite formations from uranium-rich areas such as the southwest. Such formations are covered with uranium-rich overburden. In some places, high levels of uranium together with inorganic sediment, sand, dirt, and other impurities extend downward into the lignite formation.

Extraction, combustion, gasification and/or liquefaction of such a resource can result in the release of trace quantities of radioactive substances. Radioactivity monitoring should be included in the ambient monitoring plan for all synfuels plants. Depending on the concentration of radioactive isotopes in the feedstock (coal, oil shale, or tar sands), an increased emphasis on radioactivity monitoring might be warranted for some sites.

5.4.4 Arid Environments

Synthetic fuel development in the West will occur largely in arid or semi-arid areas lacking substantial amounts of uniformly distributed water. Synfuels facilities will require large amounts of process water, and the heat and pressures required for processing cause additional water loss through evaporation. These water losses could have a significant long term impact on ground/surface water flows, pollutant mobility and transformation, and diversity of natural biota near project sites. Detection of such effects may require increased emphasis on the ancillary monitoring of meteorological conditions such as humidity, solar and terrestrial radiation, and precipitation, and on the monitoring of terrestrial effects.

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The methods summarized in this appendix are grouped in four categories:

- Sampling - general methods for sample acquisition and sample conditioning.
- Preparative - techniques for the isolation of species for analysis, or to convert the sample to a form suitable for analysis.
- Analysis - procedures by which chemical species, classes or groups of compounds are quantified or qualitatively identified.
- Test - methods which measure a physical property, characteristic or effect.

Each method summary contains (where applicable):

- Title
- Analyte - components, classes of compounds, or characteristics for analyses or test methods
- Description - brief, general discussion of the method
- Application - appropriate streams or sample types for the method
- General Method Parameters - more detailed description of method, reagents, equipment and implementation. These details are given only for generally applicable, standardized methods and may not be appropriate for all sample matrices or laboratory situations.

- Limitations - known common interferences or problems that may be encountered. The detailed procedures referenced contain more extensive listings or discussions of limitations.

- Sensitivity - the general range of precision of the technique or instrumental detection limit.

- External Cost - the estimated cost range for an outside contractor or service laboratory to provide a single analytical determination, to implement a preparative procedure or test method for one sample, or to collect a single sample. Travel or freight expenses are not included.

- Internal Cost - 1) the estimated manhour range required within the owner/operator organization for the completion of a single analysis, test, preparative procedure or sample collection.
  2) the estimated cost range for the acquisition of instruments and equipment required to perform sampling, analysis, preparation or test methods.

- References - information sources necessary for review prior to protocol selection and implementation. Primary references contain specific information which rigorously defines each procedure.

- Alternates - method title and reference for well known alternative approaches which may be required by the sample matrix or data needs.

The cost and sensitivity of the techniques are of such general interest that they may require further explanation. The external costs are the costs estimated for an external (independent) organization to perform specific tasks. These estimates cover a range from the cost for straightforward implementation of the method to the cost for a complex sample or implementation requiring procedure validation. The external cost estimate also covers the range from a single sample basis (more expensive) to the cost per sample on a multiple sample basis when economy of scale is a factor. The external cost range is relatively broad in many cases, but it should cover most situations.

The internal costs cover the estimated range of manhours necessary for the work to be performed within the owner or operators facility by his staff. Like the external cost range, internal labor estimates cover both straightforward and complex situations and single or multiple determinations. The manhours given in internal costs cannot be compared directly to the external cost. External costs reflect not only a labor rate which varies with the level of skill required by the technique, but also the various overhead burdens that associated equipment costs would generate for each method. The estimated range of capital equipment costs that the owner/operator would incur to provide internal facilities for sampling, and analysis are given as additional internal costs.

The sensitivity of each method is presented as the imposed instrumental detection or precision limit. Many analytical techniques contain steps to allow for sample dilution or concentration. Many of the sampling techniques allow collection of larger samples to give more total sample mass for analysis. Therefore it is difficult, if not misleading, to supply minimum detectable quantities in terms of stream concentrations. As a guide, however, Table A-1 gives example relationships between instrument mass detection limits, stream concentrations and illustrative sample volumes.

The majority of the suggested methods are widely used standard techniques. The techniques for gaseous streams rely heavily upon Title 40 of the Code of Federal Regulations, Part 60, which contains stationary source

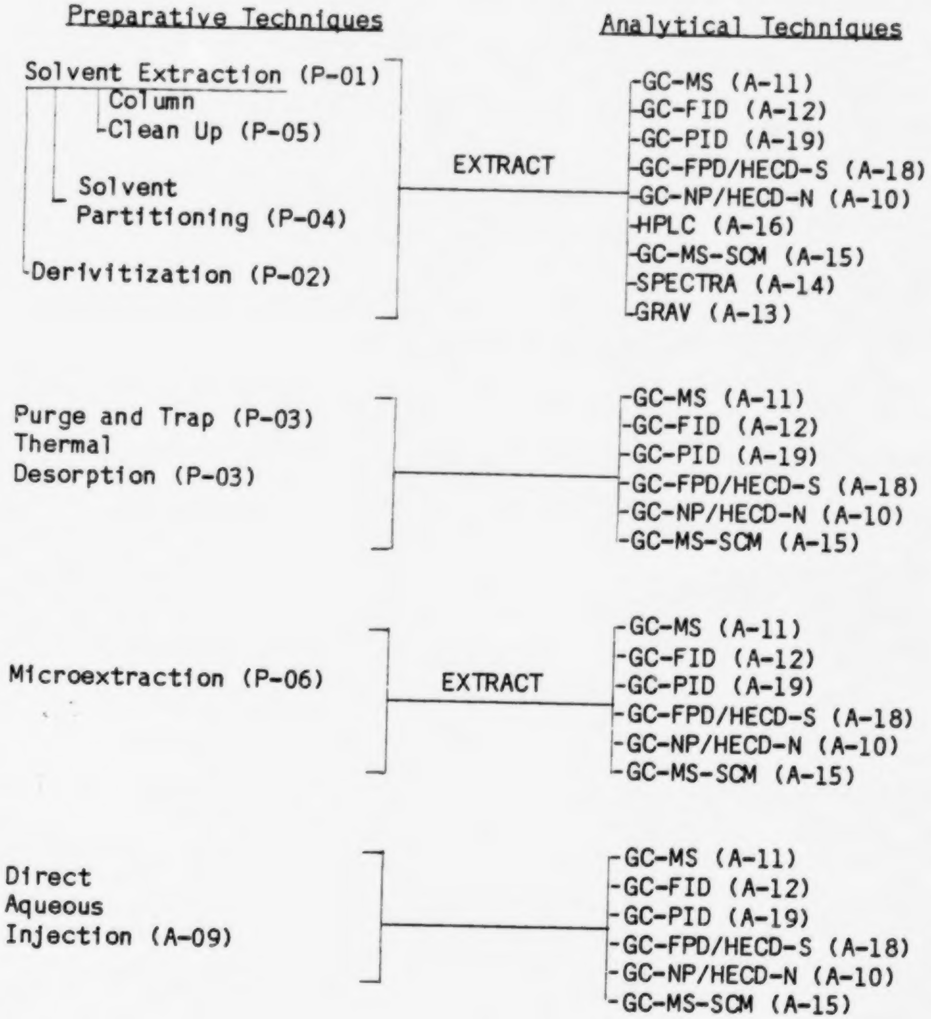
TABLE A-1. EXAMPLE STREAM CONCENTRATIONS FROM DETECTION LIMITS AND SAMPLE VOLUMES

Detection Limit	Sample Volume	Stream Concentration
Gaseous*		
1-10 ng	1 Nm^3	0.5-5 ppt (v/v)
1-10 ng	100 Nm^3	50-500 ppt (v/v)
10-100 ng	100 Nm^3	0.5-5 ppb (v/v)
10-100 ng	1 mL	5-50 ppm (v/v)
10-100 μg	100 Nm^3	0.5-5 ppm (v/v)
10-100 μg	1 L	5-50 ppm (v/v)
Liquids		
1-10 ng	10 mL	0.1-1 ppb (w/v)
1-10 ng	1 L	1-10 ppt (w/v)
10-100 μg	1 L	10-100 ppb (w/v)
10-100 mg	1 L	10-100 ppm (w/v)
Solids		
10-100 ng	1 g	10-100 ppb (w/w)
1-10 mg	1 g	0.1-1% (w/w)
10-100 μg	1 kg	10-100 ppb (w/w)
1-10 μg	10 g	0.1-1 ppm (w/w)

*Assume MW ~ 50.

emissions sampling and analysis methods. The IERL-RTP Procedures Manual: Level I Environmental Assessment was used as a primary reference for sampling, preparative and analysis techniques for non-regulated components. Most of the methods suggested for liquid streams are in the Federal Register (vol. 44, no. 233, December 3, 1979) which cites the 1975 edition of Part 31 of the American Society for Testing and Materials (ASTM) Annual Book of ASTM Standards, the American Public Health Association 14th edition of Standard Methods for the Examination of Water and Wastewater and the EPA Methods of Chemical Analysis of Water and Wastes. The methods suggested for solid streams are primarily ASTM techniques. Methods for analysis of solids, after preparative ashing or digestion, follow the aqueous analytical techniques outlined above. The suggested analytical techniques for organic species from aqueous and solid samples also follow the Federal Register (vol. 44, no. 233, December 3, 1979).

Some cross-references to sampling, preparative and analytical methods are included in the method descriptions. Many combinations can be made between preparative options for organics and organic analysis techniques, as shown in Figure A-1.



( ) Method number for general description of technique

Figure A-1. Organic Preparative and Analytical Technique Associative Flow-Chart

METHOD NUMBER: S-01

SAMPLING METHOD: Solid Waste Streams

DESCRIPTION: There are several variations of sampling appropriate for solid waste. The simplest is simple random sampling which is accomplished by collecting a one-time grab sample. If the stream is stratified, a number of grab samples or a cross section such as a coring technique should be used to collect a representative sample of the stratifications (unless only a particular part of the stream is of interest). If the stream varies or is stratified and an "average" sample is needed, systematic random sampling is required. The final variation of grab sampling is composite sampling which is systematic grab sampling as a function of time or location with a resultant summation (compositing) of samples for the designated time period. Compositing can be accomplished by a combination of mixing and random splitting of the total material from the grab samples.

APPLICATIONS: Any of the sampling methods described above may be appropriate; the method is selected according to the testing objective and homogeneity of the stream. Systematic random and composite sampling provide an average sample which is sometimes required for compliance testing and provide a statistically defensible sampling approach. In most instances, composite sampling is the method of choice, unless the stream is known to be homogeneous with respect to the components of interest. A stream should be presumed to be heterogeneous, especially with respect to low level (<500 ppm) components, unless there are data to the contrary. However, if a stream is known to be essentially constant in composition, a simple random sampling may be as representative as systematic or composite sampling. A series of simple grab samples, also, is appropriate when a significant change in an effluent stream needs to be monitored to define variation in effluent composition. Various sampling devices are available for different physical forms and sample consistencies.

SAMPLING METHOD PARAMETERS: One of the following three typical solid sampling devices and procedures will usually be applicable.

Thief (Grain) Sampler: The thief is inserted into the solid to be sampled, the inner tube rotated to open the sampler, and then agitated to encourage flow of the sample. The sampler is closed and the sample withdrawn. A thief sampler is useful for powdered or granular solids. It has limited utility when the solid diameter is greater than 0.6 cm.

Trowel (Scoop): The trowel is constructed from stainless steel or a polypropylene scoop. Prior to collecting a sample, the top half-inch of the solid must be removed. Kg-sized samples are obtained by combining subsamples taken at several locations. The trowel is generally used for dry materials and surface soil. It is not applicable to sampling deeper than 8 cm. Obtaining reproducible samples is sometimes difficult.

Trier (Sample Corer/Waste Pile Sampler): The sample corer (trier) is fabricated from PVC pipe or sheet metal as described in SW-846. (The waste pile sampler is a larger version.) The sampler is inserted into the solid material at an angle of 0-45°, rotated to cut a core of the solid or sludge, and removed with the concave side upward. The trier is also applicable to powdered or granular material.

REPRESENTATIVE ALIQUOTS FROM FIELD SAMPLES: Field samples are composited in order to obtain representative aliquots for analysis. Procedures for compositing solids and sludges are given as follows:

Sludges: Samples are homogenized and aliquots removed. Aliquots are then combined and mixed.

Solids: If necessary, the sample is ground to reduce the particle size (20 mesh screen) using agate or alumina equipment. The sample is then riffled through a steel or aluminum riffler; appropriate aliquots are combined, cone-blended three times or roll-blended by an auger, and coned and quartered.

LIMITATIONS: With many solid waste streams, heterogeneity in the sample makes obtaining a representative sample difficult. Since solids are often sluiced, the compositions of the solids are also affected by leaching during processing causing compositional variability in the samples for analysis. For sluiced solid streams, the procedures described under liquid waste sampling (Methods S10, S11) will generally be applicable. Some solid wastes will change in composition upon long exposure to air. While major constituents may be constant for most solids, trace species may vary greatly.

SENSITIVITY: The sensitivity of solid waste sampling will vary with stream characteristics and sampling program. Sensitivity is determined by both sample size and the analytical finish used. Typically, for metals analyzed by ICAP, a mg/kg concentration range in the solid sample can be expected to be detectable. For organics, detection limits on the order of 10 mg/kg should be generally attainable. These levels assume that approximate kg size samples are collected and that 10-100 g aliquots are taken for analysis.

QA/QC: All field samples should be collected in replicate. Duplicates of simple random grab samples or of field composites are the minimum acceptable. At least one sample from each pair will be analyzed; the second will serve as a contingency sample in the event of breakage or of apparently anomolous analysis results on the first sample. If stream heterogeneity is expected to be a major problem, three or more replicates should be collected and analyzed separately. At least one blank should be generated for each set of samples. This will generally be a field blank, consisting of appropriate sample container(s), taken to the field and handled (container opened, contents transferred, etc.) like the samples. If contamination from the field environment is expected to be a major problem, a trip blank should be prepared in addition to the field blank. The trip blank consists of sample container(s) taken to the field, unopened, and returned to the laboratory for analysis. Comparison of trip and field blanks allows assessment of contamination from the field environment vs. that due to shipment, storage, or post-sampling laboratory work-up.

REQUIREMENTS FOR ANALYTICAL TECHNIQUES: Generally, solids should be analyzed as soon as possible following collection. If vapors from solids are part of the analytes, solids must be stored in glass bottles to prevent diffusion through plastic. For greatest compositional stability, samples should be stored at 4°C, in the absence of air. Generally, chemical preservation is unnecessary. However, for solids containing large liquid fractions, filtrations or other separation of phases on-site may be required to maintain the original phase of components. Typically, sample aliquots for organic analysis are stored in borosilicate glass containers with Teflon-lined screw caps, and the aliquots for volatile organic analysis are stored so that there is no headspace above the sample. Sample aliquots for inorganic analysis may be stored in high-density, linear polyethylene containers. Specific sample collection techniques and preservation are listed with individual analyte test methods, and these steps should be performed according to analytes of interest.

METHOD NUMBER: S-01

EXTERNAL COST:

Preparation for Simple Grab Sample: per single sample	$30-$100
Preparation for Systematic Grab Sample: per single sample	$700-$1500
Preparation for Composite Grab Sample: per single sample	$700-$1500

INTERNAL COST:

Preparation for Simple Grab Sample: manhours/sample	2-8
Preparation for Systematic Grab Sample: manhours/sample	24-48
Preparation for Composite Grab Sample: manhours/sample	24-48

Capital Equipment:

Grain Sampler	$100-$500
Trier (Sample Corer/Waste Pile Samples)	$50-$200
Trowels, Dipper	$10-$30
Pumps (Slurry Sampling)	$200-$500
Shovel	$20
Grinder	$100-$6,000
Auger	$100-$200
Riffler	$50-$200

PRIMARY REFERENCE: U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, "Test Methods for Evaluating Solid Waste--Physical/Chemical Methods," SW-846, Washington, D.C., 1982

ADDITIONAL REFERENCES: American Society for Testing and Materials, Philadelphia, Pennsylvania, "Annual Book of ASTM Standards," Method No. E-300-37, Parts 29 and 30, 1973

METHOD NUMBER: S-01

Berl, W.G. (ed.), Physical Methods in Chemical Analysis, Academic Press, New York, Vol. III, 183-217, 1956

Kennedy, W.R. and J.F. Woodruff (eds)., Symposium on Sampling Standards and Homogeneity, Los Angeles, California, June 25-30-, 1972, American Society for Testing and Materials, Philadelphia, Pennsylvania, 1973

METHOD NUMBER: S-02

SAMPLING METHOD: Sampling for Determination of Vapor Phase Moisture

DESCRIPTION: A known volume of gas is passed through a knock-out to remove entrained water, and then a silica gel trap to determine moisture content gravimetrically.

APPLICATIONS: This sampling method is applicable to gaseous streams, with a wide range of pressures and temperatures, in which moisture determinations are needed.

SAMPLING METHOD PARAMETERS: The silica gel is weighed prior to sampling. A known volume of sample is drawn through a tared silica gel trap. The trap is then reweighed on a high capacity analytical balance and the amount of absorbed species determined. A knockout must be used upstream of the silica gel trap to remove entrained water.

LIMITATIONS: Hydrogen sulfide or organic species sorption may bias data if either are present in appreciable concentrations. The method may yield questionable results when applied to saturated gas streams that contain water droplets.

SENSITIVITY: Weight gains of 1% can be measured with some accuracy.

QA/QC: A blank portion of silica gel not used for sampling should be weighed as a control. The balance used should be calibrated regularly. Use of indicating silica gel is strongly recommended to insure that the capacity of the drying tube is not exceeded.

The length of sampling lines should be minimized to prevent condensation losses, and the silica gel trap be cooled to a temperature of 68°F or less.

METHOD NUMBER: S-02

EXTERNAL COST:

Per single sample	\$3--\$60

INTERNAL COST:

Manhours/sample	0.5-1
Capital Equipment:	
Analytical Balance	\$1,000-\$2,000
Pump, Meter	\$3,000

PRIMARY REFERENCE: Tital 40 Code of Federal Regulations, Part 60, Appendix A, 1980. [Method 4 - Determination of Moisture Content in Stack Gases]

METHOD NUMBER: S-03

SAMPLING METHOD: Isokinetic Collection of Particles from Gas Streams to Determine Mass Loading (Grain Loading) or Particle Size Distribution

DESCRIPTION: The gas sample is obtained at the same flow rate as that occurring within the process pipe or duct (the isokinetic rate). The particles are removed by filtration or by dynamic particle sizing devices such as an impactor or a series of cyclones. Cross-sectional area of probe orifice (nozzle) and acquisition rate may be varied to cover a wide range of stream velocities. Sample collection device and sample transport lines are heated to remain above dew point of gas stream sampled.

APPLICATIONS: Generally applicable to a wide range of process pressures and temperatures.

LIMITATIONS: Streams at elevated temperatures and pressures will require modifications of general techniques. Access to the flowing stream for determination of velocity profile and point of average velocity or traversing to average stratification is required. Aerosol tars and oils will be collected if present. Entrained moisture, if vaporized in the collection device, may leave salt residues that bias results. Non-isokinetic sampling rates produce bias in particle loading or size distribution determination.

SENSITIVITY: Mass collected must be sufficient for accurate gravimetric results, 10-100 g is the lower level of detection. Gas volumes can be measured to 0.1 scf with accuracy.

QA/QC: Determination of stream velocity profile, temperature, pressure, moisture content and volumetric flow rate must be made prior to sample acquisition (EPA Methods 1, 2, 3 and 4, reference 1). Calibration of gas metering equipment, pitot tubes, temperature probes and equipment leak check are necessary.

EXTERNAL COST:

Per single sample	$500-$2500 (depending on particulate concentration)

INTERNAL COST:

Manhours/single sample	2-12 (depending on particulate concentration)

Capital Equipment:

Probe, console, meter, pump	$10,000-$20,000
Probe, high volume pump, metering system	$25,000-$50,000

PRIMARY REFERENCE: Title 40, Code of Federal Regulations, Part 60, Appendix A, 1980. [Method 5 - Determination of Particulate Emissions from Stationary Sources]

Accurex, Aerotherm. Operating and Service Manual. Mountain View, CA. April, 1976.

ALTERNATE REFERENCE:

Lentzen, D. E., D. E. Wagoner, E. D. Estes and W. F. Gutknecht, "EPA/IERL-RTP Procedures Manual: Level 1 Environmental Assessment, Second Edition," EPA-600/7-78-201 (January 1979), NTIS No. PB 293795/AS.

METHOD NUMBER: S-04

SAMPLING METHOD: Removal of Moisture

DESCRIPTION: Devices for removal of vapor phase moisture are used upstream of particulate sampling devices for protection of equipment or minimization of interferences. In some cases, knockout traps are used for removal of water in aerosol form.

APPLICATIONS: Vapor phase moisture removal by desiccants is appropriate for the protection of gas sampling and metering equipment. Condensation is appropriate immediately after resin collection and prior to gas scrubbing by impingers. Dilution and permeation are recommended as "polishing techniques" when gas streams must be sufficiently dry for introduction into continuous on-line analyzers. For fixed gases, entrained moisture is usually removed by placing a knockout prior to sample collection.

GENERAL METHOD PARAMETERS: Desiccants (e.g., silica gel, drierite) may be packed into a tube or cartridge inserted upstream of the device to be protected, for collection of vapor phase water. Knockout traps for water in aerosol form may be similarly inserted. Permeation-type dryers may be used, especially with on-line instrumental methods of analysis.

LIMITATIONS: Choice of device is dependent upon species of interest, and a different sampling train may be necessary. Desiccants may absorb some of the components of interest as well as the water vapor. Knockout traps may also remove some species if they are condensable in the same temperature range as water. Permeation devices may be permeable to some species other than water (e.g., ammonia) resulting in non-quantitative recovery of those compounds.

METHOD NUMBER: S-04

QA/QC: Leak check each device per manufacturer's instructions.

EXTERNAL COST:

Per single sample	\$15-\$30

INTERNAL COST:

Manhours/sample	1-2
Capital Equipment:	
Permeation drier	\$500-\$2,000

PRIMARY REFERENCE: Fougler, B.E., and P.G. Simmonds, "Drier for Field Use in the Determination of Trace Atmospheric Gases," Anal. Chem., 51(7):1089-1090, June 1979

METHOD NUMBER: S-05

SAMPLING METHOD: Vapor Phase Organics Collection by Sorbent Trapping

DESCRIPTION: Gas stream is passed through a cartridge or canister filled with porous polymeric resin beads or granules. Vapor phase organics are sorbed by the resin. Both XAD-2 resin (for moderately volatile compounds) and Tenax-GC resin (for volatile compounds) are very widely used. Additionally, XAD-8, Carbotrap, Carboseive, and the Chromosorbs have been used successfully as have other less common sorbents. Specific sorbent traps are recently available for nitrosamines.

APPLICATIONS: Broad range of volatile organic compounds are collected. Generally, highly polar compounds are sorbed less efficiently. The technique is effective to collect organics present at low levels; large gas volumes can be concentrated for analysis of very low stream concentrations.

PREPARATIVE REQUIREMENTS: Gas stream should be cooled (∿20°C), particles/aerosols removed (S-06) and free of entrained moisture (S-04). Resins should be cleaned (appropriately for the recovery technique, extraction or thermal desorption) prior to use.

LIMITATIONS: Low organic content streams (<100 ppb) require long sampling times (high gas volumes) for accumulation of sufficient mass for analysis. If aqueous or organic condensates are produced by gas clean-up/condensation, aliquots must be analyzed in an analogous manner to the resin catch for an accurate determination of total vapor phase stream composition.

SENSITIVITY: Technique sensitivity primarily a function of analytical detection technique (see introduction, Table A-1).

QA/QC: Collected sample may be spiked for recovery data. Significant problems exist in accomplishing accurate spiking of the stream to determine sorption efficiency. Collection efficiency can be determined by serial collection and multiple analyses. Resin blank analyses are required. Collection system must be rigorously cleaned prior to sampling. Good sampling practices, leak check, meter calibration, accurate volume measurement, must be followed. Well mixed or representative sample recommended.

EXTERNAL COST:

Per single sample	\$500-\$3000 (depending on sample volume)

INTERNAL COST:

Manhours/sample	1-12 (depending on sample volume)

Capital Equipment:

Probe, meter, console, pump	\$10,000-\$15,000
High-volume sampling system	\$30,000-\$40,000

PRIMARY REFERENCE: Lentzen, D. D., D. E. Wagoner, E. D. Estes and W. F. Gutknecht. EPA/IERL-RTP Procedures Manual: Level 1 Environmental Assessment, Second Edition. EPA-600/7-78-201, USEPA, RTP, NC, January 1979. [NTIS No. PB 293795/AS].

BIBLIOGRAPHY: Title 40, Code of Federal Regulations, Part 60, Appendix A, 1980. [Method 1 - Sample and Velocity Traverse for Stationary Sources, Method 2 - Determination of Stack Gas Velocity and Volumetric Flow Rate].

Gallant, R. F., J. W. King, P. L. Levins, and J. F. Piecewicz. Characterization of Sorbent Resins For Use in Environmental Sampling. EPA-600/7-78-054, USEPA, RTP, NC, March 1978.

METHOD NUMBER: S-06

SAMPLING METHOD: Particle/Aerosol Removal from Gas Streams

DESCRIPTION: Particulate removal is achieved by filtration, use of cyclones, or electrostatic precipitation. If the particles are not to be retained for analysis, isokinetic collection or access to traverse the stream are unnecessary.

APPLICATIONS: This method is used whenever a particular sampling device or procedure requires a particulate-free gas stream sample. Particulate removal is necessary for most on-line monitors of gaseous species. Particulate material is also removed prior to collection of vapor phase materials in impingers or solid sorbent devices.

SAMPLING METHOD PARAMETERS: A filter, cyclone, or electrostatic precipitator is inserted into the sampling train upstream of the device to be protected.

LIMITATIONS: Tar or soil aerosols can rapidly plug filter surfaces. Electrostatic precipitation may be more effective for these situations. Extremely high particle loadings may require high capacity filters (large surface area or thimbles) to avoid frequent changes or unacceptable pressure drop. Particulate removal devices may also remove some fraction of the species sought.

QA/QC: Preliminary consideration must be given to the possibility that some of the analyte of concern may be removed by the particluate removal device. It may be possible to ascertain this from first principles. In cases where there is doubt, however, (for example, when sampling acid gases from a stream that may contain alkaline particulate material), it will be necessary to conduct laboratory experiments to confirm that the quantitative collection of the species sought is not affected by the particulate removal device.

EXTERNAL COST:

Per single analysis	$250-$2,500 (depending on removal technique)

INTERNAL COST:

Man-hours/sample	1-12 (depending on removal technique)
Capital Equipment:	
Filter holder	$75-$300
Cyclones	$600-$3,000
Electrostatic precipitator	$2,000-$8,000

PRIMARY REFERENCE: Lentzen, D.E., D.E. Wagoner, E.D. Estes, and W.F. Gutknecht. EPA/IERL-RTP Procedures Manual: Level 1 Environmental Assessment, Second Edition. EPA-600/7-78-201, USEPA, RTP, NC, January 1979 [NTIS No. PB 293795/AS]

ADDITIONAL REFERENCE: Title 40, Code of Federal Regulations, Part 60, Appendix A, 1980. [Method 5 - Determination of Particulate Emissions from Stationary Sources]

METHOD NUMBER: S-07

SAMPLING METHOD: Collection of Vapor Phase Samples by Liquid Trapping (Impinger Collection)

ANALYTE: HCN, NH_3, NO_x, minor and trace elements, radioactive species, H_2S, SO_2, HCl, HF, some organic components.

DESCRIPTION: The gas stream is passed through a series of impingers which contain aqueous solutions of specific reagents (see Table 1 for specifics and subdesignations S-07A, S-07B, etc.) to sorb or react with a target vapor phase component. Solutions are kept cool to provide increased collection efficiency. The vapor phase specie can be concentrated in the impinger solutions by increasing the total volume of gas sampled.

APPLICATIONS: Applicable to a wide range of stream temperatures and pressures. Full access to traverse the stream is not required although samples obtained at a point of average velocity or from a well mixed stream are recommended. Vapor phase organics can be trapped in solvent solutions.

PREPARATIVE REQUIREMENTS: Entrained moisture or condensable organics which could be collected in the impingers must be removed by prior condensation or impaction if analytical interferences are a potential. Particles/aerosols should be filtered from the gas stream prior to sample collection (S-06). Impinger solutions should be prepared and preweighed under the best laboratory conditions available prior to sampling. Commonly used sorption solutions are listed in Table 1.

LIMITATIONS: General limitations and comments for collection of specific analytes are given in Table 1. The limitations of impinger collection techniques in general are 1) the difficulty involved in preparing a spiked gaseous stream to verify technique applicability and assess the potential of unanticipated interferences; 2) serial collection, and multiple analyses are required to determine the collection efficiency of the

TABLE 1. COMMON TRAPPING SOLUTIONS FOR IMPINGER SAMPLE COLLECTION

S-07 Subdesignation	Analyte	Solution	Comments
A	HCN	5% Sodium Hydroxide	Final solution pH must be <10 to avoid poor retention of HCN. High CO_2 (<20%) will produce sodium carbonates which can cause pluggage, poor gas-liquid contact, decreased solution pH. Not selective for HCN.
		10% Calcium Hydroxide	Calcium carbonate solids from high CO_2 (<20%) cause fewer collection and handling problems than the sodium carbonates from NaOH collection. Final solution pH must be <10. Not selective for HCN.
		10% Sodium Acetate	Applicable to CO_2-rich streams, solids formation hindered by buffering. Final solution pH must be <10. Not selective for HCN.
B	NH_3	5% Sulfuric Acid	Other acids also applicable. Final solution pH influences retention of ammonia. Other basic species sorbed also.
C	NOx	Saltzman Solution [glacial acetic acid, sulfanilic acid, N-(1-naphthyl) ethylene diamine dihydrochloride]	Possibly non-stoichiometric reaction see (A-41). EPA Method 7 (evacuated bomb) more generally recommended.
D	Minor & Trace Elements, Radioactive Species	H_2O_2, Ammonium persulfate/ silver nitrate	Multi-reagent impinger series, most applicable to combusted streams, silver and sulfur cannot be determined due to solution composition
		10% Nitric acid, deionized water	Multi-reagent impinger series,
E	H_2S	Peroxide, $CdSO_4$	Multi-reagent impinger series, appropriate for low levels of H_2S (EPA Method 11)
		2% Zinc Acetate	ZnOAc preferable for high levels of sulfide, oxidation losses occur at low levels. $CdSO_4$ (above) more appropriate to low levels.
		$Cd(OH)_2$	Like Method 11 (above) appropriate for low level H_2S
F	SO_2	80% Isopropanol, 3% hydrogen peroxide	Multi-reagent impinger series, free ammonia interferes (EPA Method 6)
		Potassium tetrachloromercurate	Modified West-Gaeke method, solutions thermally unstable above 4°C
G	HCl	2% NaOH	Carbonate formation in high CO_2 streams causes handling difficulties, effects solution pH. Other caustics applicable if necessary.
H	HF	2% NaOH	Carbonate formation in high CO_2 streams causes handling difficulties, effects solution pH. Other caustics applicable if necessary.
		SPADNS/Zirconium Lake	EPA Method 13
I	Phenols	0.1 N NaOH	Carbonate formation in CO_2-rich streams can cause sampling difficulties and alter solution pH. Not specific for phenolics, heavily substituted phenols not collected efficiently. Other caustics applicable.
J	Formaldehyde	Sodium tetrachloromercurate	Modification of West-Gaeke technique.

technique; and 3) the potential for analyte loss or compositional changes to occur during gas clean-up, filtration, moisture or condensate removal, prior to analyte collection.

SENSITIVITY: Vapor phase detection levels detemined by analysis techniques: HCN (A-28), NO_x (A-41), minor and trace elements (A-40), radioactive species (A-36), H_2S (A-29), SO_2 (A-35), HCl (A-33), and HF (A-31) or as given by EPA methods cited. Very large gas sample volumes may be obtained to determine very low stream concentrations.

QA/QC: Good sampling practice requires accurate measurement of volumes, impinger collection techniques require low flow rates (0.1-0.5 scfm for 500 ml impingers) to allow adequate gas-liquid contact. Equipment leak check and meter calibrations are necessary. Solution blanks must be retained for analysis.

EXTERNAL COST:

Per single sample	\$500-\$2500 (depending on stream concentration)

INTERNAL COST:

Manhours/sample	1-12 (depending on stream concentration)

Capital Equipment:

Probe, pumps, meter, console	\$8,000-\$12,000

PRIMARY REFERENCES: Scarengellis, F. P., B. E. Saltzman, and S. A. Frey. Spectrophotometric Determination of Atmospheric Sulfur Dioxide. Anal. Chem. 39 1967. pp. 1709-1719.

Title 40, Code of Federal Regulations, Part 60, Appendix A, 1980. [Method 6 - Determination of Sulfur Dioxide Emissions from Stationary Sources, Method 7 - Determination of Nitrogen Oxide Emissions from Stationary Sources, Method 11 - Determination of Hydrogen Sulfide Content of Fuel Gas Streams in Petroleum Refineries, Method 13 - Determination of Total Fluoride Emissions from Stationary Sources, SPADNS Zirconium Lake Method].

Lentzen, D. D., D. E. Wagoner, E. D. Estes and W. F. Gutknecht. EPA/IERL-RTP Procedures Manual: Level 1 Environmental Assessment, Second Edition. EPA-600/7-78-201,USEPA, RTP, NC, January 1979. [NTIS No. PB 293795/AS].

ALTERNATIVE REFERENCES: Title 40, Code of Federal Regulations, Part 60, Appendix A, 1980. [Method 15 - Determination of Hydrogen Sulfide, Carbonyl Sulfide, and Carbon Disulfide Emissions from Stationary Sources; Method 16 - Semicontinuous Determination of Sulfur Emissions from Stationary Sources; Method 20 - Determination of Nitrogen Oxides, Sulfur Dioxide, and Oxygen Emissions from Stationary Gas Turbines].

USEPA. Proposed Rules. Federal Register, 46(117):31905-31909, June 18, 1981. [Method 16A - Determination of Total Reduced Sulfur Emissions from Stationary Sources].

USEPA. Proposed Rules. Federal Register, 46(25):11498-11500, February 6, 1981. [Appendix I - Determination of Sulfur Dioxide Emissions from Fossil Fuel Combustion Sources (Continuous Bubbler Method)].

USEPA. Proposed Rules. Federal Register, 46(16):8359-8364, January 26, 1981. [Performance Specification 2 - Specifications and Test Procedures for $SO^{\sim}$ and NOx Continuous Emission Monitoring Systems in Stationary Sources].

USEPA. Proposed Rules. Federal Register, 46(138):37289, July 20, 1981. [Performance Specification 5 - Specifications and Test Procedures for TRS Continuous Emission Monitoring Systems in Stationary Sources].

BIBLIOGRAPHY: Leithe, W. and A. Ailver-Humphrey. 1970. The Analysis of Air Pollutants. Science Publishers, London.

Lyles, G. R., F. B. Dowling and V. J. Blanchard. Quantitative Determination of Formaldehyde in the Parts-per-100 Million Concentration Level. J. Air Pollution Control Assoc., 15, 1965.

METHOD NUMBER: S-08

SAMPLING METHOD: Fugitive Screening for Hydrocarbons

DESCRIPTION: Vapor phase sample is pulled into the analyzer by a small pump and the hydrocarbon concentration determined without speciation by flame ionization detection.

APPLICATIONS: Samples may be obtained from open or semi-open sources or in vicinity of potential leak sources (valves, flanges, etc.).

SAMPLING METHOD PARAMETERS: After the vapor phase sampler is allowed to stabilize, the instrument is calibrated using an appropriate calibration gas of known concentration. The probe inlet of the sampler is then placed at the surface to be monitored. The probe is moved along the interface until a maximum meter readout is obtained. The probe inlet is held at the maximum reading location for approximately two times the instrument response time. Results are usually reported as parts-per-billion.

LIMITATIONS: A total detector response is obtained; sample components are not separated and quantified as separate species. Response of the FID is reasonably uniform for hydrocarbons; response for compounds containing oxygen or other hetero-elements is more variable. Pulling of variable amounts of dilution air from the ambient environment can affect the quantitative validity of the measurements.

SENSITIVITY: 10 ppb-100 ppm depending on instrument and attenuation capabilities.

QA/QC: Frequent calibrations and analysis of known blends must be performed.

METHOD NUMBER: S-08

EXTERNAL COST:

Per single sample	$10-$20

INTERNAL COST:

Man-hours/sample	∿0.1
Capital Equipment	
Portable FID	$4,000-$6,000

PRIMARY REFERENCES: USEPA. Title 40, Code of Federal Regulations, Part 60, Appendix A. December 5, 1980. [Method 25 - Determination of Total Gaseous Organic Concentration Using a Flame Ionization Analyzer]

USEPA. Proposed Rules. Federal Register, 45(224). December 17, 1980. [Method 25A, Method 25B]

METHOD NUMBER: S-09

SAMPLING METHOD: Collection of Vapor Phase Organics in Impingers.

ANALYTE: Acidic, basic or reactive organic species.

DESCRIPTION: A measured volume of gas is collected in a solution containing an appropriate solution (e.g., dilute caustic for acidic compounds).

APPLICATIONS: This method is used for organic species that are not efficiently collected on solid adsorbent sampling devices. Examples are highly polar organic acids and bases or reactive species such as formaldehyde.

SAMPLING METHOD PARAMETERS: Impingers containing appropriate reagents are inserted into a sampling train (See Method S-03). For organic acids, 0.1-1 N HCl is appropriate. For organic bases, 0.1-1 N NaOH may be employed. For formaldehyde, an acidic solution of 2,4-dinitrophenylhydrazine is used.

LIMITATIONS: Specific solutions must be selected for each group of compounds to be collected. The collection efficiency for various species can be highly variable and must be validated. Use of organic solvents for collection of neutral organic species is a technique formerly used, but generally inferior to use of solid adsorbents.

REQUIREMENTS FOR ANALYTICAL TECHNIQUES: Samples may require solvent extraction after a treatment step to free the organic moiety (e.g., pH adjustment).

QA/QC: Good sampling practice requires accurate measurement of gas volume. The sampling system should be constructed to prevent organic contamination, e.g., Tygon tubing, greases, plasticware cannot be used. Spike studies should be performed by spiking the impinger solution and sampling zero grade air to determine loss during sampling.

EXTERNAL COST:

Per single sample	$250-$1,000 (depending on stream concentration)

INTERNAL COST:

Man-hours/sample	2.5 - 10 (depending on stream concentration)
Capital Equipment: Probe, pumps, meter, console, glassware	$5,000-$10,000

PRIMARY REFERENCE: Arthur D. Little, Inc. Sampling and Analysis Methods for Hazardous Waste Incineration. EPA Contract No. 68-02-3111, USEPA, February 1982.

METHOD NUMBER: S-10

SAMPLING METHOD: Composite Sample Collection from Aqueous Streams

DESCRIPTION: Composite samples may be collected either as a series of manual grab samples or by continuous automatic sampling. Either flow proportional sample collection or time compositing of individual samples can be done. The frequency of collection must be determined. If an automated sampler is utilized, the collection rate is determined from the compositing time and total sample volume required.

APPLICATIONS: This technique is applicable when it is desirable to mix several individual samples to determine the average representative composition of a stream or to minimize the number of samples to be analyzed.

SAMPLE METHOD PARAMETERS: Samples are collected as described in Method S-11. Samples are homogenized and an aliquot removed. Appropriate aliquots are combined and mixed in a container.

LIMITATIONS: The composite sampling approach does not provide information concerning the variability of stream composition. Preservation reagents or cooling may be required to avoid sample degradation during long compositing periods (P-11).

QA/QC: All field samples should be collected in replicate. Duplicates of simple random grab samples or of field composites are the minimum acceptable. At least one sample from each pair will be analyzed; the second will serve as a contingency sample in the event of breakage or of apparently anomolous analysis results on the first sample. If stream heterogeneity is expected to be a major problem, three or more replicates should be collected and analyzed separately. At least one blank should be generated for each set of samples. This will generally be a field blank, consisting of appropriate sample container(s), taken to the field and handled (containers opened, contents transferred, etc.) like the samples. If contamination from the field environment is expected to be a major problem, a trip blank should be prepared in addition to the field blank. The trip blank consists of sample container(s) taken to the field, unopened, and returned to the laboratory for analysis. Comparison of trip and field blanks allows assessment of contamination from the field environment vs. that due to shipment, storage, or post-sampling laboratory work-up.

EXTERNAL COST:

Per single sample	$200-$800

INTERNAL COST:

Man-hours/sample	2-10
Capital Equipment:	
Automatic samplers	$1,000-$2,000

PRIMARY REFERENCES: USEPA Technology Transfer. Handbook for Monitoring Industrial Wastewater, Washington, DC, August 1973.

USEPA-EMSL. Handbook for Sampling and Sample Preservation of Water and Wastewater. EPA-600/4-82-029, Cincinnati, OH, September 1982.

METHOD NUMBER: S-11

SAMPLING METHOD: Grab Sample Collection from Aqueous Streams

DESCRIPTION: Grab samples may be collected manually or automatically from the water stream using a pump or other suitable device. The grab sample volume required depends upon the total number of separate analyses that must be made; however, for a detailed characterization, a 4-liter sample is usually sufficient.

APPLICATIONS: The technique is applicable to aqueous streams providing that there is a long residence time in a vessel or pond or that stream characteristics are relatively constant. Multiple grab samples taken over time provide a means to determine stream variability. Grab samples are recommended for analysis of components which may be lost or degraded during long compositing periods.

SAMPLING METHOD PARAMETERS:

Preparative Requirements: Clean bottles for collection and appropriate reagents and equipment for on-site preparation and preservation (P-11).

Method:

Tap: A sample line is inserted into the collection vessel. The sample line and bottle must be thoroughly rinsed with the liquid stream prior to isolating the sample. (This material must be disposed of in an appropriate manner.) A sample is collected over a sampling time which exceeds 5 minutes.

Weighted Bottle: A stoppered bottle is lowered to the appropriate depth, the stopper removed, and a sample collected. After the bottle is filled, the sample bottle is capped and wiped off.

Dipper (Pond Sampler): The beaker inserted into the liquid with the opening downward, until the desired depth is reached. The beaker is then turned right side up, filled with sample, the dipper raised, and the sample transferred to a storage vessel. A 2-4 L sample is collected.

Coliwasa Sampler: The Coliwasa sampler is inserted in the closed position into the liquid. The sampler is then opened, filled, capped, and removed.

LIMITATIONS: A grab sample may not be representative of the average stream conditions over time. Grab samples may not provide a representative sample of suspended solids from a stream in which solids stratification is prevalent.

QA/QC: All field samples should be collected in replicate. Duplicates of simple random grab samples or of field composites are the minimum acceptable. At least one sample from each pair will be analyzed; the second will serve as a contingency sample in event of breakage or of apparently anomolous analysis results on the first sample. If stream heterogeneity is expected to be a major problem, three or more replicates should be collected and analyzed separately. At least one blank should be generated for each set of samples. This will generally be a field blank, consisting of appropriate sample container(s), taken to the field and handled (container opened, contents transferred, etc.) like the samples. If contamination from the field environment is expected to be a major problem, a trip blank should be prepared in addition to the field blank. The trip blank consists of sample container(s) taken to the field, unopened, and returned to the laboratory for analysis. Comparison of trip and field blanks allows assessment of contamination from the field environment vs. that are due to shipment, storage, or post-sampling laboratory work-up.

METHOD NUMBER: S-11

EXTERNAL COST:

Per single sample	\$20-\$200 (depending on access to stream)

INTERNAL COST:

Man-hours/sample	0.5-8 (depending on access to stream)
Capital Equipment: Pump, sample lines, general equipment	\$200-\$400

PRIMARY REFERENCES: USEPA Technology Transfer. Handbook for Monitoring Industrial Wastewater. Washington, DC, August 1973.

USEPA-EMSL. Handbook for Sampling and Sample Preservation of Water and Wastewater. EPA-600/4-82-029, Cincinnati, OH, September 1982.

ADDITIONAL REFERENCES: U.S. Environmental Protection Agency/Office of Solid Waste, Washington, DC, "Test Methods for Evaluating Solid Waste - Physical/Chemical Methods," SW-846 (1980).

deVera, E. R., B.P. Simmons, R.D. Stephens and D.L. Strom, "Samplers and Sampling Procedures for Hazardous Waste Streams," EPA-600/2-80/018 (January 1980), NTIS No. PB80-1355353.

American Society for Testing and Materials, Philadelphia, Pennsylvania, "Annual Book for ASTM Standards," Method D-270 (1975).

American Society for Testing and Materials, Philadelphia, Pennsylvania, "Annual Book of ASTM Standards," Method E-300 (1973).

METHOD NUMBER: S-12

SAMPLING METHOD: Collection/Determination of Vapor Phase Components by Solid Adsorption.

DESCRIPTION: Gas sample is pulled through commercially-available, specific sorbent-filled tubes. Sorbents selectively react with specific components of interest. Widely used for CO, H_2S, NH_3, HCN.

APPLICATIONS: Fugitive emission sampling, atmospheric pressure streams, and general screening.

SAMPLING METHOD PARAMETERS:

Method: A gas sample is collected through a sorbent tube at a flow rate of 1 L/min.

LIMITATIONS: This technique is generally not applicable to pressurized streams. Tubes are generally not available for high level components or high capacity sampling. Tubes are usually not quantitative. The gas matrix should be evaluated for interferences for each species of interest and sorbent.

SENSITIVITY: 1-100 ppm depending on tube reagents, analyte and gas sample volume.

QA/QC: Tubes must be protected from breakage and contamination. Field blanks must be verified for potential degradation or contamination.

METHOD NUMBER: S-12

EXTERNAL COST:

Per single sample	$10-$50

INTERNAL COST:

Man-hours/sample	0.2-1
Capital Equipment:	
Small volume pump and tubes	$300-$700

PRIMARY REFERENCE: USHEW, Public Health Service, Center for Disease Control, National Institute of Occupational Safety and Health. The Industrial Environment--Its Evaluation and Control, 1973, pp. 188-195.

METHOD NUMBER: S-13

SAMPLING METHOD: Collection of Vapor Phase Samples for Direct Analysis (Bag or Bomb Collection).

DESCRIPTION: The gas sample is collected at low flow rates from a pressurized stream or pumped into an inert bag (Teflon, Tedlar, polyethylene) equipped with a shut-off valve. Glass sample bombs may be either previously evacuated and filled, or at atmospheric pressure and purged to atmospheric or slight positive pressure Atmospheric pressure bombs must be purged with 8-10 residence volumes prior to sample collection. High pressure steel bombs provide larger sample volumes and are durable.

APPLICATIONS: Generally applicable to a range of process pressures if pressure reduction and flow control are included upstream of sample container.

SAMPLING METHOD PARAMETERS:

Preparative Requirements: Sample should be dry and particle/aerosol free prior to collection (S-04, S-06).

Method:

Gas Bag (Used for Unreactive Gases): The probe on the gas bag is inserted into the center of the sample source and a sample is collected.

Gas Bulb (Used for Reactive Gases): A gas bulb is purged with the gas to be sampled prior to isolating the sample. The bulb is then re-evacuated, the valve opened, a gas sample collected, and the valve closed.

METHOD NUMBER: S-13

LIMITATIONS: Some polymeric bags lose light gaseous species (e.g., hydrogen) by diffusion. Reactive species may be lost if inert bags or pre-passivated glass bombs are not employed. Condensable species are not recovered from the bag or bomb. Condensates or particles/aerosols provide sorption surfaces and active sites for reactive species. Metallic sample bombs may provide active sites and loss of reactive species. Metal carbonyls may be formed in situ if metal sample bombs are used for streams containing carbon monoxide at high pressure.

SENSITIVITY: Volumes generally from 2 L to 10 L can be collected unless pressurized steel bombs are used. 10 psig is maximum pressure for glass bombs. Steel bombs are available for pressures up to 3,000 psig.

QA/QC: In addition to general good sampling practice, bombs or bags must be rigorously cleaned and analytically checked for background contamination prior to use.

EXTERNAL COST:

Per single sample	\$30-\$100

INTERNAL COST:

Man-hours/sample	0.5-2
Capital Equipment:	
Probe, drier, pump, regulators	\$500-\$1,000
Glass bombs or bags	\$20-\$100
Steel bombs	\$100-\$500

METHOD NUMBER: S-13

PRIMARY REFERENCES: Lentzen, D.E., D.E. Wagoner, E.D. Estes, and W.F. Gutknecht. EPA/IERL-RTP Procedures Manual: Level 1 Environmental Assessment, Second Edition. EPA-600/7-78-201 USEPA, RTP, NC, January 1979, [NTIS No. PB 293795/AS]

USEPA. Proposed Rules. Federal Register, 45(77):26682, April 18, 1980. [Method 110 - Determination of Benzene from Stationary Sources]

USEPA. Title 40, Code of Federal Regulations, Part 60, Appendix A. December 5, 1980. [Method 3 - Gas Analysis for Carbon Dioxide, Oxygen, Excess Air and Dry Molecular Weight]

METHOD NUMBER: S-14

SAMPLING METHOD: Collection of Fugitive Emissions by Bagging

DESCRIPTION: Fugitive emissions from a point source are collected by enclosing the source in a flexible inert bag (Tedlar, Teflon, etc.). The concentration in the bag can be increased by collection over time or most often by pulling ambient air over the source and into the bag. The bag contents may then be analyzed as a vapor phase sample.

APPLICATIONS: Discrete sources of such size or location as to be practically and reliably enclosed.

SAMPLING METHOD PARAMETERS: The probe on the gas bagging equipment is inserted into the center of the source and a sample is collected.

LIMITATIONS: Some sources cannot be enclosed. Levels of components close to ambient background are not reliably quantified. Condensation of the components of interest within the bag biases data.

QA/QC: Good sampling practices dictate that the bag and any materials that contact the bag be clean and not introduce bias or interferences. Background levels must be determined.

EXTERNAL COST:

Per single sample	$75-$250

METHOD NUMBER: S-14

INTERNAL COST:

Man-hours/sample	1-3
Capital Equipment: Small pump, meter, bagging material	$1,000-2,000

PRIMARY REFERENCES: Title 40, Code of Federal Regulations, Part 61, Appendix B, 1980. [Method 106 - Determination of Vinyl Chloride from Stationary Sources]

USEPA. Proposed Rules. Federal Register, 45(77):26677-26682, April 18, 1980. [Method 110 - Determination of Benzene from Stationary Sources]

METHOD NUMBER: S-15

SAMPLING METHOD: Collection of Fugitive Particulate Emissions

DESCRIPTION: High volume sample acquisition of ambient air within the industiral site is employed using a prepared glass filter for the collection of ambient airborne particulate material. Sample can be collected for both mass loading or chemical characterization. A split stream may be passed through a condensor or resin canister.

APPLICATIONS: Technique can be utilized in a grid pattern to profile a site, upwind/downwind of an emission source or in any required alternate site locations. Appropriate for fugitives of open or semi-open origin.

SAMPLING METHOD PARAMETERS: An EPA-approved high-volume sampling system is used for collection of particulate material. If collection of organics is also required, an IERL/RTP Fugitive Assessment Sampling Train (FAST) may be substituted. Samples of ambient air are drawn through the train at a sampling rate of 5 cu ft/hr or greater. Careful location of sampling devices in upwind/downwind locations is required. In order to allow interpretation of the data, meteorological information must be collected during the sampling period.

LIMITATIONS: Long term sampling (8 hours or more) required for collection of sufficient mass for chemical characterization. The FAST sampling is bulky, and requires a trailer. A modified standard hi-vol sample requires a filter change whenever a 10% reduction in flow (from design criteria) is observed.

QA/QC: Good sampling practices and routine checks on collector operation are sufficient.

METHOD NUMBER: S-15

EXTERNAL COST:

Per single sample	\$500-\$1,000 (depending on duration of sampling)

INTERNAL COST:

Man-hours/sample	10-40 (depending on duration of sampling)
Capital Equipment:	
FAST Sampling System	\$2,000-\$10,000
Hi-Vol Sampler (unmodified)	<\$1,000

PRIMARY REFERENCES: Kolnsberg, H. Technical Manual for the Measurement of Fugitive Emissions. EPA 600/2-76-089-A Wethersfield, CT, 1976.

Lentzen, D.E., D.E. Wagoner, E.D. Estes, and W.F. Gutknecht. EPA/IERL-RTP Procedures Manual: Level 1 Environmental Assessment, Second Edition. EPA-600/7-78-201, USEPA, RTP, NC, January 1979. [NTIS No. PM 293795/AS]

METHOD NUMBER: P-01

PREPARATIVE METHOD: Solvent Extraction of Moderately Volatile Organics

DESCRIPTION: Organic species are removed from a solid or liquid sample matrix by extraction with a suitable solvent. A drying step through Na_2SO_4 and a concentration step is usually required to remove water and enrich the organic content in the solvent.

APPLICATIONS: This preparation method is used in combination with GC, HPLC, GC/MS, MS, IR and is applicable to gas samples collected on sorbents and impingers and to solids, sludges, organic liquids, and aqueous samples.

DRYING AND CONCENTRATING: Sample extracts are passed through anhydrous Na_2SO_4 and may subsequently be concentrated by evaporative techniques (Kuderna Danish). Concentration or dilution of a sample extract prior to further analysis, such as GC/MS, may be determined by such techniques as TCO (A-12) and GRAV (A-13).

LIMITATIONS: The extraction efficiency depends on the solvent selected, the sample matrix, and the organic functional groups present. Solvents other than methylene chloride may be used if preliminary laboratory data suggests that all organic species are not being extracted optimally. Solvents should also be selected on the basis of compatibility with the detector used for analysis. Possible alternatives are diethyl ether for acidic organics and hexane for non-polar species. The extract may require additional treatment to remove interferences and/or increase sensitivity, derivatization (P-02), solvent on column separation (P-05) before analysis.

SAMPLING REQUIREMENTS: Samples should be stored in glass, stainless steel or Teflon® containers to minimize contamination and should be kept cold (4°C) to minimize degradation. Relatively large volumes of sample (1-3 L of water, 1-2 kg of solids) are required to extract detectable quantities of low level organic components.

QA/QC: Preliminary QC should check the method using standards. The recovery and precision should be calculated. As ongoing QC, blanks (reagent and method), blank spikes, matrix spikes, and matrix replicates are extracted with every sample set.

Samples should be extracted within a short time to minimize degradation.

EXTERNAL COST:

Per single sample	\$50-\$200

INTERNAL COST:

Manhours/sample	1-8

Capital Equipment:

Specialized glassware and related lab equipment	\$1,000-\$5,000 (typical start-up cost)

REFERENCES: US EPA, Office of Solid Waste and Emergency Response. Test Methods for Evaluating Solid Waste--Physical/Chemical Methods. SW-846. Washington, D.C., 1982

Method Number: P-01

Arthur D. Little, Inc. Sampling and Analysis Methods for Hazardous Waste Combustion. EPA Contract No. 68-02-3111, US EPA, February 1983

Radian Corporation. Assessment, Selection and Development of Procedures for Determing the Environmental Acceptability of Synthetic Fuel Plants Based on Coal, May 1977 (NTIS FE-1795-3)

Keith, L.H. ed. Identification and Analysis of Organic Pollutants in Water. Ann ArborScience, Ann Arbor, MI, 1977

METHOD NUMBER: P-02

PREPARATIVE METHOD: Derivatization of Organic Compounds in Sample Extracts.

DESCRIPTION: By chemical reaction with a derivatization reagent, polar or high boiling organic compounds are changed into species which are more easily analyzed (e.g., converting a carboxylic acid into a methyl ester). This technique can also be used to add a functional group to a compound which enables selective detection. For example, phenols can be fluorinated to allow gas chromatographic detection by electron capture with an increase in sensitivity over flame ionization detection.

APPLICATIONS: This preparation method can be used in combination with HPLC, GC, and GC/MS analysis techniques. It is generally used to reduce interferences, increase sensitivity, or shorten analysis time. Of the species expected to be important in synfuel plant effluents, aldehydes and carboxylic acids are the two categories most likely to require derivatization; most others can be analyzed as is. Procedures for derivatizing aldehydes and carboxylic acids are given below.

GENERAL METHOD PARAMETERS:

Derivatization of Aldehydes: Aldehydes are derivatized using dinitrophenylhydrazine (DNPH) prior to extraction, and analysis by GC/MS, GC or HPLC. A sample aliquot is taken for derivatization/extraction. If the matrix is a DNPH impinger reagent which has been used for collection of aldehydes, it is immediately extracted with methylene chloride and n-pentane. If the sample is an aqueous liquid such as a scrubber water or an extract prepared from a waste stream or comprehensive stack sampling train, it is treated by mixing with DNPH reagent (2,4-dinitrophenylhydrazine in 2N HCl) for 10 minutes prior to extraction. After extraction, the combined methylene chloride/pentane layers are washed with 2N HCl and then distilled water. The extracts are then evaporated to dryness and the residue dissolved in acetonitrile. These solutions are analyzed as the DNPH derivatives of the aldehydes by GC/MS or by HPLC procedures.

Derivatization of Carboxylic Acids: Carboxylic acids are esterfied prior to analysis by GC or GC/MS. After the sample is extracted into methylene chloride, the extract is transferred through a funnel plugged with glass wool into a (K-D) flask equipped with a 10 mL graduated receiver with liberal washings of solvent. The acids in the extract are esterified using either diazomethane or boron trifluoride.

Diazomethane: The extract is evaporated to <5 mL. An aliquot of diazomethane is added to the extract. The mixture stands for 10 minutes with occasional swirling and subsequently rinsed with diethyl ether.

Boron Trifluoride: An aliquot of benzene is added to the extract. The extract and benzene are evaporated to a small volume. The ampule is removed and further concentrated using a two-ball micro-Snyder column. After cooling, boron trifluride methanol reagent is added to the benzene solution. This mixture is held at 50°C for 30 minutes on the steam bath. After cooling, neutral 5% sodium sulfate is added and the flask stoppered, shaken and allowed to stand for three minutes for phase separation. The solvent layer is transferred to a small column packed with sodium sulfate over florisil adsorbent and eluted with benzene. The final eluent volume is adjusted with benzene. The extracts are analyzed as the methyl esters of the carboxylic acids using GC/MS or GC procedures.

LIMITATIONS: Sufficient quantity of reagent must be added to completely derivatize the analytes. This can only be determined by analyzing samples spiked before derivatization to determine percent recovery.

QA/QC: Preliminary QC should check the method using standards. The recovery and precision should be calculated. As ongoing QC, blanks (reagent and method), blank spikes, matrix spikes, and matrix replicates are derivatized with every sample set.

EXTERNAL COST:

Per single analysis	\$5-\$200

INTERNAL COST:

Man-hours/sample	0.1-10
Capital Equipment:	
Specialized glassware, reagents, general laboratory equipment	\$50-\$1,000 (depending on equipment availability in existing laboratory)

PRIMARY REFERENCES: Radian Corporation. "Assessment, Selection, and Development of Procedures for Determining the Environmental Acceptability of Synthetic Fuel Plants Based on Coal," Austin, TX, May 1977 [NTIS FE-1795-3]

U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. "Test Methods for Evaluating Solid Waste Physical/Chemical Methods," Washington, DC, July 1982, 2nd Edition.

Arthur D. Little, Inc. "Sampling and Analysis Methods for Hazardous Waste Combustion." EPA Contract No. 68-02-3111, U.S. Environmental Protection Agency, February 1983.

Keith, L.H., ed. "Identification and Analysis of Organic Pollutants in Water," An Arbor Science, Ann Arbor, MI, 1977.

Kuwata, K., M. Uebori, and Y. Yamasaki, "Determination of Aliphatic and Aromatic Aldehydes in Polluted Airs as their 2,4-Dinitrophenylhydrazones by High Performance Liquid Chromatography." J. Chromatogr. Sci., 17, 264-268 (1979).

Smith, A.E., "Uses of Acetonitrile for the Extraction of Herbicide Residues from Soils." J. of Chrom., 129, 309-314 (1976).

METHOD NUMBER: P-03

PREPARATIVE METHOD: Thermal Desorption of Volatile Organic Species

DESCRIPTION: The sample which has been trapped cryogenically or on a suitable sorbent is thermally desorbed into the analytical instrument. For aqueous and solid samples a purging step onto a trap is required to remove the volatile organics from the sample matrix. In general, the method is appropriate for non-polar compounds with boiling points of 150°C or less (e.g., benzene, xylenes). This range can be extended by higher desorption temperatures and longer purge and desorption times to include compounds such as naphthalene and pyridine.

APPLICATIONS: For gas samples collected on sorbents, the method is applicable to only species which are retained on the sorbent and can be thermally desorbed. For aqueous and solid samples, the method is further limited by the ability to purge the compound from the sample matrix.

LIMITATIONS: This method requires a series of sample handling steps which can be labor and equipment intensive as compared to microextraction (P-06). These handling steps may also produce some analytical difficulties due to the complexity of the method. Contamination from volatile species in the sample container or in the room air is a major concern. The purging and desorption times and temperatures must be carefully optimized to allow measurement of the higher boiling volatile species such as benzene and xylene while preventing loss of the highly volatile species.

QA/QC: Frequent blanks should be analyzed to insure uncontaminated system due to carryover from previous analytes. Back-up sorbent traps (serial samples) should be analyzed to determine analyte break-through. Good laboratory practice is essential. Spiking studies are recommended.

SAMPLING REQUIREMENTS: Sorbent samples should be in sealed tubes and stored in a freezer until the time of analysis. The technique does not allow for re-analysis, therefore duplicate samples are required. Also, sorbent samples should be collected at various gas volumes (e.g., 1 mL, 50 mL, 1000 mL) if the concentration of analytes is unknown. Aqueous samples (5-50 mL) should be collected in glass vials with no headspace.

EXTERNAL COST:

Per single sample	\$20-\$250

INTERNAL COST:

Manhours/sample	0.5-4
Capital Equipment:	
Thermal desorption unit	\$2,000-\$10,000

PRIMARY REFERENCES: Bellar, T. A., and J. J. Lichtenberg. Determining Volatile Organics in Microgram-per-Litre Levels by Gas Chromatography. J. American Water Works Assoc., 66(12): 739-744, December 1974.

USEPA. Proposed Rules. Federal Register, 44(233): 69468-69478, December 3, 1979. [Method 601 - Purgable Halocarbons, Method 602 - Purgable Aromatics]

ALTERNATE REFERENCES: Arthur D. Little, Inc. Sampling and Analysis Methods for Hazardous Waste Incineration. Cambridge, MA, February 1982.

USEPA, Office of Solid Waste and Emergency Response. Test Methods for Evaluating Solid Waste Physical/Chemical Methods. Washington, D.C., July 1982.

METHOD NUMBER: P-03

Keith, L.H., ed. Identification and Analysis of Organic Pollutants in Water. Ann Arbor Sciences, Ann Arbor, MI, 1977

Keith, L.H., ed. Advances in the Identification and Analysis of Organic Pollutants in Water. Ann Arbor Science, Ann Arbor, MI, 1981

REFERENCE: Miller, H.C., R.H. James and W.R. Dickson, "Evaluated Methodology for the Analysis of Residual Wastes," Report prepared for U.S. Environmental Protection Agency/Effluent Guidelines Division, Washington, D.C., by Southern Research Institute, Birmingham, Alabama under Contract No. 68-02-2685 (December 1980)

U.S. Environmental Protection Agency, Federal Register, 44, 69464-69575 (December 3, 1979)

METHOD NUMBER: P-04

PREPARATIVE METHOD: Solvent Partitioning of Semivolatile Organics

DESCRIPTION: Solvent partitioning is used as a cleanup procedure prior to analysis in order to eliminate interferences and potential erroneous results. Organic species are separated by pH adjustment and/or selection of appropriate solvents e.g., phenols can be separated from neutral species.

APPLICATION: This preparation method can be used in combination with GC, HPLC and GC/MS analysis techniques and it is generally useful for isolating a particular category of organics (e.g., phenols) from a sample containing other organic sepcies, therefore reducing interferences. This method should be considered when: (1) the organic species of interest are at low concentrations relative to the other organics, i.e., 10 ppb of phenanthrene in a sample containing 10 ppm phenol, or (2) the analytical method is non-specific, e.g., GC-FID (A-12) and many other organic species could interfere. This method should be considered an extension of the general solvent extraction method (P-01).

GENERAL METHOD PARAMETERS:

Organic Acids and Bases: An aliquot of the sample extract or organic liquid is shaken with an aqueous solution at pH 12-13 to extract organic acids and/or at pH 2 to extract organic bases into the aqueous phase. The pH of the aqueous phase is then readjusted to pH 2 in the case of acids and/or to pH 12-13 for bases. The aqueous phase is then reextracted with a solvent, such as methylene chloride as described in Method P-01.

Neutral Species: An aliquot of the sample extract or organic liquid is shaken with a non-miscible organic solvent such as acetonitrile. The organic phase containing the compound of interest is separated and concentrated if necessary.

LIMITATIONS: Selection of a solvent system that will achieve the desired class separation(s) can be difficult. All steps of the procedure must be validated by spiking into the sample matrix. This procedure can be labor intensive and may not be necessary for relatively clean sample extracts or for analytical techniques with sufficient specificity, such as GC/MS (A-11), nitrogen-specific detection (A-10), sulfur-specific detection (A-18), etc.

QA/QC: Preliminary QC should check the method using standards. The recovery and precision should be calculated. As ongoing QC, blanks (reagent and method), blank spikes, matrix spikes and matrix replicates are extracted with each sample set.

EXTERNAL COST:

Per single analysis	\$20-\$200

INTERNAL COST:

Man-hours/sample	1-10
Capital Equipment:	
Specialized glassware and related lab equipment	\$1,000-\$5,000 (typical start-up cost)

PRIMARY REFERENCES: U.S. EPA, Office of Solid Waste and Emergency Response. Test Methods for Evaluating Solid Waste Physical/Chemical Methods. Washington, DC, July 1982, Method 3530.

Radian Corporation. Assessment, Selection and Development of Procedures for Determining the Environmental Acceptability of Synthetic Fuel Plants Based on Coal. Austin, TX, May 1977. [NTIS FE-1795-3].

Miller, H.C., R.H. James and W.R. Dickson, "Evaluated Methodology for the Analysis of Residual Wastes," Report prepared for U.S. Environmental Protection Agency/Effluent Guidelines Division, Washington, DC, by Southern Research Institute, Birmingham, Alabama, under Contract No. 68-02-2685 (December 1980).

McKown, M.M., J.S. Warner, R.M. Riggen, M.P. Miller, R.E. Heffelfinger, B.C. Garrett, G.A. Jungclaus, and T.A. Bishop, "Development of Methodology for the Evaluation of Solid Wastes." Report prepared for U.S. Environmental Protection Agency/Effluent Guidelines Division, Washington, DC, by Battelle Columbus Laboratories, Columbus, OH, under Contract No. 68-03-2552 (January 1981).

U.S. Environmental Protection Agency, Federal Register, 44, 69464-69575 (December 3, 1979).

METHOD NUMBER: P-05

PREPARATIVE METHOD: Organic Fractionation by Column (Sorbent) Separation

DESCRIPTION: The sample extract is eluted through a column containing sorbent to selectively separate classes of organic species. The most commonly used sorbents are alumina, florisil and silica gel. Ion exchange chromatography and gel permeation chromatography (GPC) are related techniques which are used in special cases.

APPLICATIONS: This method is used to isolate a particular organic group, e.g., PNAs, from a sample extract (P-01). Compound separation is generally based on polarity. This method is very useful for "clean-up" of extracts prior to analysis by non-specific methods such as GC-FID (A-12), and provides an additional measure of reliability in identification.

LIMITATIONS: Some compounds can irreversibly absorb on the column. The elution time of the compound group of interest must be established. Separation can be effected in samples containing high concentrations of organic species.

SENSITIVITY: Column techniques range from macro (capable of fractionating grams of sample) to micro (capable of fractionating 1-2 mg of sample).

QA/QC: Sorbents must be reproducibly conditioned (activated). The activation of each lot should be checked by a standard. The sorbent can generate artifacts; blanks are essential.

EXTERNAL COST:

Per single sample	$25-$200

METHOD NUMBER: P-05

INTERNAL COST:

Manhours/sample	2-10 (depending on ease of fractionation)
Capital Equipment:	
Glass columns	$50-$200
Fraction collector	$1,000-$6,000

REFERENCES:

Arthur D. Little, Inc. Sampling and Analysis Methods for Hazardous Waste Combustion. EPA Contract No. 68-02-3111, US EPA, February 1983.

US EPA, Office of Solid Waste and Emergency Response. Test Methods for Evaluating Solid Waste-Physical/Chemical Methods. SW-846. Washington, DC, 1982.

Keith, L.H., ed. Identification and Analysis of Organic Pollutants in Water. Ann Arbor Science, Ann Arbor, MI, 1977.

Keith, L.H., ed. Advances in the Identification and Analysis of Organic Pollutants in Water. Ann Arbor Science, Ann Arbor, MI 1981.

Radian Corporation. Assessment, Selection and Development of Procedures for Determining the Environmental Acceptability of Synthetic Fuel Plants Based on Coal. Austin, TX, May 1977 [NTIS FE-1795-3].

Lentzen, D.E., D.E. Wagoner, E.D. Estes and W.F. Gutknecht, "EPA/IERL-RTP Procedures Manual: Level 1 Environmental Assessment (second edition) "EPA-600/7-78-201 (October 1978). NTIS No. PB293795/AS.

U.S. Environmental Protection Agency, Federal Register, 44, 69464-69575 (December 3, 1979).

Miller, H.C., R.H. James and W.R. Dickson, "Evaluated Methodology for the Analysis of Residual Wastes," Report prepared for the U.S. Environmental Protection Agency/Effluent Guidelines Division, Washington, DC, by Southern Research Institute, Birmingham, Alabama, under Contract No. 68-02-2685 (December 1980).

METHOD NUMBER: P-06

PREPARATIVE METHOD: Microextraction

DESCRIPTION: A small amount of an organic solvent is mixed with the sample (e.g., 100 mL of an aqueous sample with 1 mL of solvent). The solvent extract containing the organic species generally requires no further concentration prior to analysis.

APPLICATIONS: This preparation method is used in combination with GC, GC/MS and HPLC analysis techniques. This method is useful for the long-term monitoring of compounds with high partition coefficients and which have been identified previously; it can be used for most solid and liquid samples. For example, the method has been used for determining the following: volatiles in water, phenols in water, PNAs collected on filters, and benzene collected on charcoal. Because the method is not labor or equipment intensive, it is well suited for field and/or long-term analyses.

GENERAL METHOD PARAMETERS: Aqueous: Surrogates are added to an aliquot of the sample saturated with Na_2SO_4. The sample is then transferred to a volumetric flask. Hexane (for neutral organics) or diisopropylether (for acidic organics) is added to the flask inverted on a mechanical shaker and the content shaken. The contents are allowed to settle and the measured sample extract is transferred to a labeled container.

Filters and sorbents: Surrogates are added to the filter or sorbent. The sample is then extracted with a small amount of solvent, typically using sonification.

LIMITATIONS: Microextraction may not recover the analytes as efficiently as the solvent extract procedures (Method P-01) due to low sample-to-solvent ratio. When using microextraction as compared to P-01, the solvent is usually not further concentrated, thus volatility losses are decreased, and few interferences are extracted.

SENSITIVITY: Other preparative procedures such as solvent extraction (P-01) or thermal desorption (P-03) will probably allow for better sensitivity, assuming the same analytical detection technique is employed.

QA/QC: Preliminary QC should check the method using standards. The recovery and precision should be calculated. As ongoing QC, blanks (reagent and method), blank spikes, matrix spikes, and matrix replicates are extracted with every sample set. Internal standards or surrogates are generally required for quantification.

SAMPLE REQUIREMENTS: In general, this method requires a small volume of sample, e.g., 100 mL for aqueous samples, 0.1-1 g for solid samples. The samples should be collected in glass, Teflon® or stainless steel containers to minimize contribution from other organics. Standard procedures for organic sample handling (keep cold, etc.) should be followed. Aqueous samples containing volatile analytes should be collected in sample bottles with no headspace. Other samples with volatile analytes (sorbents, solids, etc.) should be sealed to prevent loss of the volatile species.

EXTERNAL COST:

Per single sample	\$10-\$50

INTERNAL COST:

Manhours/sample	0.5-2

Capital equipment: negligible

REFERENCES: Keith, L.H., ed. Advances in the Identification and Analysis of Organic Pollutants in Water. Ann Arbor Science, Ann Arbor, MI, 1981

METHOD NUMBER: P-07

PREPARATIVE METHOD: RCRA EP Toxicity Test Extraction Method for Solids

DESCRIPTION: The Extraction Procedure (EP) Toxicity Test is designed to simulate the leaching a waste would undergo if it were disposed in an improperly designed landfill. Solid phase samples are extracted with deionized water maintained at a pH of 5 ± 0.2 using acetic acid. The extract is then analyzed for the species of interest. The Resource Conservation and Recovery Act (RCRA) stipulates subsequent eight analysis for eight metals (arsenic, barium, cadmium, chromium, lead, mercury, selenium, silver) and six pesticides (Endrin, Lindane, Methoxychlor, Toxaphene, 2,4,5-TP Silvex).

APPLICATIONS: This preparation method is used to determine the leachability of certain analytes from solid samples. The technique is applicable to solid wastes containing more than 0.5% solids. Wastes that contain less than 0.5% are not subjected to extraction, but are analyzed directly.

GENERAL METHOD PARAMETERS: If the waste contains free liquids, aliquots are filtered prior to extraction. The filtered solids are then extracted for 24 hours with aqueous acetic acid at pH 5. The solid and liquid phases are allowed to settle and the liquid portion is filtered.

Analysis of metals in leachate is accomplished by either AA or ICAP as specified in the following methods under Method A-40.

Metal	Method
Arsenic	AAS
Barium	ICAP or AAS
Cadmium	ICAP or AAS
Chromium	ICAP or AAS
Lead	AAS
Mercury	AAS
Selenium	AAS
Silver	ICAP or AAS

LIMITATIONS: The presence of acetic acid may make survey analysis for additional organics difficult.

SENSITIVITY: The leachability of each analyte varies with the sample matrix and the chemical form of the analyte in the solid.

QA/QC: Preliminary QC should check the method using standards. The recovery and precision should be calculated. As ongoing QC, blanks (reagent and method), blank spikes, matrix spikes and matrix replicates are extracted with every sample set.

SAMPLE REQUIREMENTS: Technique is applicable for all types of random or composite samples (S-01). A sample of 100 g is necessary per analysis. The sample should be representative of the waste. It must not have preservatives added to it. Samples can be refrigerated if it is determined that refrigeration will not affect the integrity of the sample.

EXTERNAL COST:

Per single sample	\$25-\$200

INTERNAL COST:

Manhours/sample	3-5
Capital Equipment:	
Extractor	$100-$1,000
Pressure filter	$400-$1,000
Compaction tester	$100-$500

REFERENCES: US EPA. Rules and Regulations. Federal Register, 45 (98): 33127-33137, May 19, 1980. Subpart C - Characteristics of Hazardous Waste, Appendix I - Representative Sampling Methods, Appendix II - EP Toxicity Test Procedure.

US EPA, Office of Solid Waste and Emergency Response. Test Methods for Evaluating Solid Waste--Physical/Chemical Methods. SW-846. Washington, DC 1982 [Method 1310].

METHOD NUMBER: P-08

PREPARATIVE METHOD: ASTM Batch Extraction of Solids

DESCRIPTION: A representative sample of the solid is mixed with 20 times its weight of water, agitated for two days and filtered. The filtrate is analyzed for the species of interest.

APPLICATIONS: This technique is applicable to all solid wastes.

GENERAL METHOD PARAMETERS:

Method: The sample is dried for 18 hours at 105°C, then cooled to room temperature in a dessicator. A representative portion of the material is placed in a container. Distilled water is added and the closed container is agitated continuously for 48 hours at 20°C. The bulk is separated from the aqueous phase by decantation, centrifugation or filtration, as appropriate. The filtrate is transferred and preserved for analysis.

LIMITATIONS: Solid is not ground or further divided in order to maintain representativeness with the actual waste. It may be difficult to obtain representative samples of solids that are very coarse.

SENSITIVITY: The leachability of components varies with sample matrix and chemical composition.

QA/QC: Preliminary QC should check the method using standards. The recovery and precision should be calculated. As ongoing QC, blanks (reagent and method), blank spikes, matrix spikes and matrix replicates are extracted with every sample set.

SAMPLING/SAMPLE HANDLING REQUIREMENTS: This technique is applicable for all types of random or composite samples (S-01). A sample of 70 g is necessary per analysis. The sample should be representative of the waste and should not have preservatives added.

EXTERNAL COST:

Per single analysis:	\$20-\$200

INTERNAL COST:

Manhour/sample	1-5
Capital Equipment:	
Pressure filter	\$400-\$1,000

PRIMARY REFERENCE: American Society for Testing and Materials. ASTM Batch Extraction Method A-1 (proposed by ASTM Committee D34 on Solid Wastes). Philadelphia, PA.

METHOD NUMBER: P-09

PREPARATIVE METHOD: Ashing, Fusion and Digestion of Solid Samples

DESCRIPTION: Solid waste is ashed and ignited. A portion is fused with NaOH and dissolved in HCl for the analysis of SiO_2 and Al_2O_3. Another portion of the ash is digested in H_2SO_4, HF, and HNO_3 and analyzed for the remaining elements (Fe_2O_3, TiO_2, P_2O_2, CaO, MgO, Na_2O, K_2O).

APPLICATIONS: This technique is applicable to solid wastes, primarily ashes and slags.

LIMITATIONS: Some losses may occur during ignition, fusion and digestion procedures.

QA/QC: Duplicates and blanks should be analyzed for all analytes.

SAMPLING/SAMPLE HANDLING REQUIREMENTS: Technique is applicable for all types of random and composite samples (S-01). The sample should be representative of the waste and stored without preservatives. Approximately 5 g of dry, ground sample are required per test.

EXTERNAL COST:

Per single sample	\$10-\$100

INTERNAL COST:

Manhours/sample	2-4

Capital Equipment:

Muffle furnace	\$500-\$2,000

METHOD NUMBER: P-09

REFERENCES: American Society for Testing and Materials. Annual Book of ASTM Standards, Part 26. Philadelphia, PA, 1975. [Method D2795 - Analysis of Coal and Coke Ash]

METHOD NUMBER: P-10

PREPARATIVE METHOD: Mixed Acid Digestion of Solid Samples

DESCRIPTION: Solid samples are brought into solution using a digestion procedure employing a mixture of acids. The sample is treated with a mixture of nitric and hydrofluoric acids and heated. Perchloric acid is added and the digestion is taken to dryness. The residue is dissolved using hydrochloric acid and diluted with deionized water to a known volume then analyzed for specific analytes.

APPLICATIONS: This technique is applicable to all solid wastes.

LIMITATIONS: No speciation of individual elements as compounds can be determined on this digest. Occasionally, losses during digestion occur to spattering behavior of solids during heating. Volatile elements may be lost during drying.

QA/QC: Duplicate determinations for digestion should be performed, and quality control measures suggested in the appropriate analytical methods should be followed. Perchloric acid should be used with extreme caution. Explosive conditions can occur.

SAMPLING/SAMPLE HANDLING REQUIREMENTS: Technique is applicable for all types of random or composite solid samples (S-01).

EXTERNAL COST:

Per single sample	$30-$150

METHOD NUMBER: P-10

INTERNAL COST:

Manhours/sample	3-5

Capital Equipment:

Hood	$500-$1,500
Oven	$200-$1,000

REFERENCES: US EPA, Office of Solid Waste and Emergency Response. Test Methods for Evaluating Solid Waste--Physical/Chemical Methods. SW-846. Washington DC, 1982 (Methods 3010, 3020, 3030, 3040, 3050, 3060).

McQuaker, N.R., D.F. Brown, and P.D. Kluckner. Digestion of Environmental Materials for Analysis by Inductively Coupled Plasma-Atomic Emission Spectrometry. Analytical Chemistry 51 (7):1082-1084, 1979.

METHOD NUMBER: P-11

PREPARATIVE METHODS: Preservation of Aqueous Samples

DESCRIPTION: Aqueous samples are preserved as soon as possible to ensure that the analytes are stabilized. In addition, holding times are usually specified to prevent decomposition of unstabilized samples prior to analysis.

APPLICATIONS: These techniques are applicable to grab (S-11) or composited (S-10) aqueous samples.

LIMITATIONS: The approach will minimize sample decomposition. Preservation is only as successful as the effort expended in rapidly stabilizing samples and completing the analyses. The proposed methods have not all been validated for maximum holding times.

GENERAL PARAMETERS: Analysis procedures are listed below along with the appropriate preservation technique.

pH Conductivity TS TDS TSS Alkalinity BOD	Samples should be stored in plastic containers at 4°C. For BOD, samples should be filtered prior to storage.
Phenolics	The pH of the sample is adjusted to less than 4 using H_3PO_4. One gram per liter of copper sulfate is added to the sample which is stored in amber glass.

COD TOC Phosphorus Ammonia Nitrite/Nitrate	The pH of the sample adjusted to less than 2 using H_2SO_4. The samples are stored in glass at 4°C. Filtration before preservation is necessary for ammonia, phosphorus, nitrate, and nitrite.
Oil and Grease	The pH is adjusted to less than 2 using HCl. The samples are stored in glass at 4°C.
Extractable Organics	Samples are stored in amber glass bottles at 4°C.
Trace Elements Radioactivity	The pH is adjusted to less than 2 with HNO_3 and the samples are stored in plastic. If necessary, filtering should be done before preservation.
Sulfide Sulfite	The sample is filtered and then preserved by addition of zinc acetate. They are stored in plastic at 4°C.
Cyanide Thiocyanate	Lead acetate is added to the samples which are then filtered. The pH is then adjusted to greater than 12 using sodium hydroxide. Samples are then stored at 4°C in plastic.
Chloride Fluoride Sulfate	No preservation is necessary.

METHOD NUMBER: P-11

SAMPLING/SAMPLE HANDLING REQUIREMENTS: A flow chart applicable to aqueous sample preservation are presented in Figure 1.

EXTERNAL COST:

Per sample set shown in Figure 1	\$25-\$100

INTERNAL COST:

Manhours/sample set shown in Figure 1	2-8
Capital Equipment	
Bottles, filtering apparatus, chemicals	\$100-\$400

REFERENCES: US EPA. Proposed Rules. Federal Register, 44(233), December 3, 1979. (Amendment to 40 CFR 136)

US EPA, Office of Technology Transfer, Methods for Chemical Analysis of Water and Wastes. EPA-625/6-74-003, Washington, DC, 1974. (NTIS No. PB 297686/AS) 298 pp. (Introduction, Tables)

American Public Health Association, American Water Works Association, and Water Pollution Control Federation. Standard Methods for the Examination of Water and Wastewater, 14th edition. APHA, Washington, DC, 1976

US EPA. Handbook for Sampling and Sample Preservation of Water and Wastewater. EPA-600/4-82-029, Cincinnati, OH, September 1982

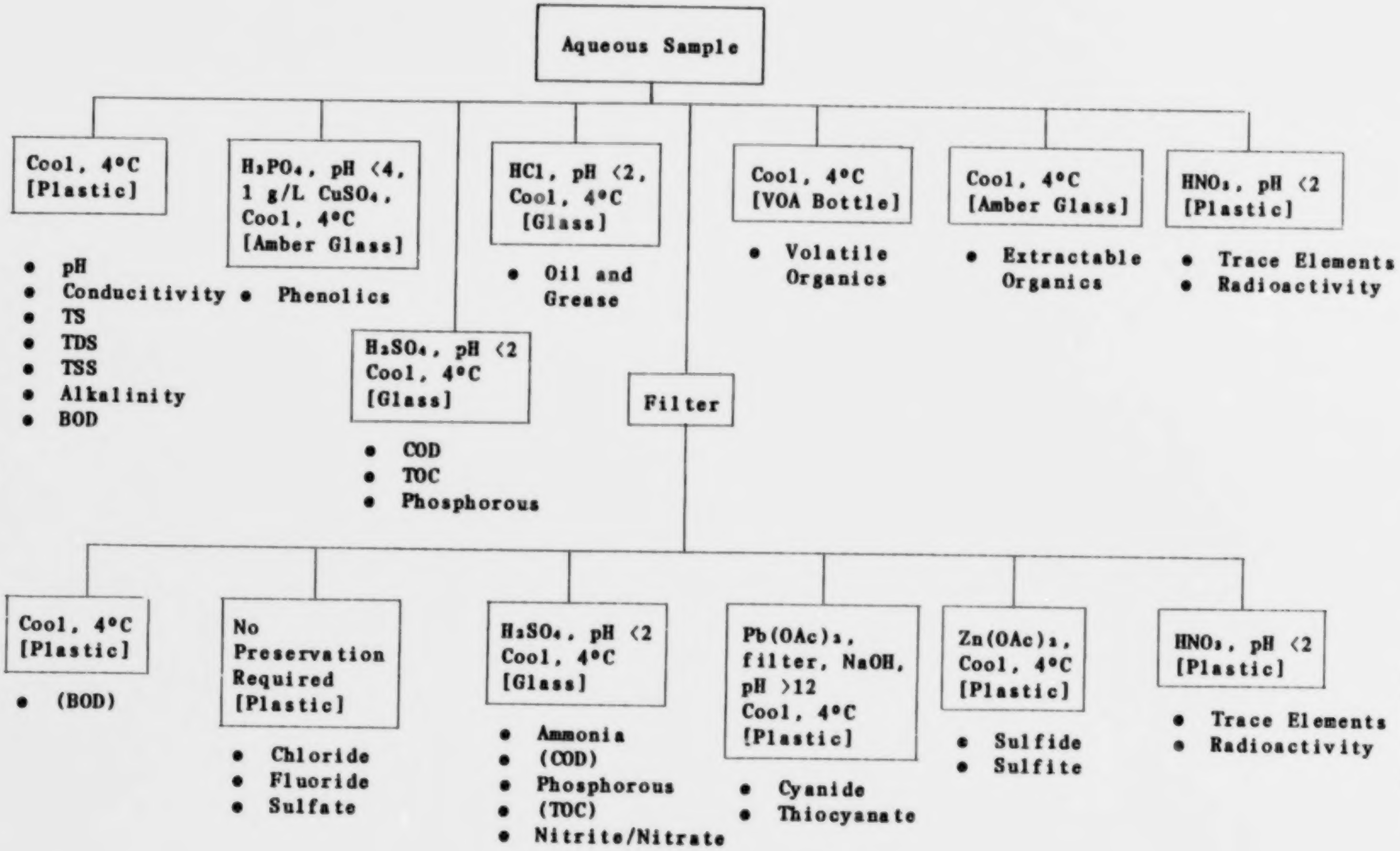


Figure 1. Preservation Procedures for Water Samples

METHOD NUMBER: P-12

PREPARATIVE METHOD: Acid Digestion for Aqueous Samples

DESCRIPTION: Aqueous samples are digested for elemental analysis (A-40) by gentle heating in the presence of HNO_3. A mixture of HNO_3 and HCl may be used.

APPLICATION: Aqueous samples and impinger solutions can be prepared for analysis by this technique.

LIMITATIONS: Volatile elemental species may be lost during digestion. Incomplete digestion may occur in samples having high organic content or high solids content.

SENSITIVITY: A minimum of 25 mL of sample is required for digestion, 100 mL of sample is generally used.

QA/QC: Preliminary QC should check the method using standards. Recovery and precision should be calculated. As ongoing QC, blanks (reagent and method), blank spikes, matrix spikes and matrix replicates are prepared with each sample set.

EXTERNAL COST:

Per single analysis	\$10-\$50

INTERNAL COST:

Manhours/sample	0.1 - 0.3
Capital Equipment:	
Hot plate, beakers	$100-$300

PRIMARY REFERENCE: U.S. Environmental Protection Agency, Office of Technology Transfer, Methods for Chemical Analysis of Water and Wastes, EPA-625/6-74-003, Washington, DC, 1974 [NTIS No. PE 2976861 AS].

METHOD NUMBER: A-01

ANALYTICAL METHOD: Gas Chromatography - Flame Photometric Detection, Vapor Phase Samples

ANALYTES: H_2S, COS, SO_2; minor volatile sulfur components: CH_3SH, C_2H_5SH, CS_2, $(CH_3)_2S$, thiophenes, etc.

DESCRIPTION: Direct injection gas chromatography using porous polymer or cyano-coated conventional or carbonaceous supports and flame photometric detection. Temperature programming usually required for separation of components. Techniques provides both quantification and speciation.

APPLICATIONS: Generally applicable to vapor phase samples of process and emission streams.

PREPARATIVE REQUIREMENTS: Gas sample should be moisture and particulate free (S-04, S-06). The presence of condensates and aerosols is also unacceptable. Sample contact with metal or plastic must be minimized or eliminated.

LIMITATIONS: Due to the reactivity of the analytes of interest, grab samples must be analyzed as soon as possible. Contact with non-passivated metal or glass surfaces should be eliminated or minimized. Contact with plastics, moisture, condensates or aerosol tars must be reduced as far as practical. Carbon dioxide causes some reduced detector response, carbon monoxide and methane cause severe reductions in detector response under most procedures. Detector linear dynamic range is limited.

SENSITIVITY: Detector linear response range usually no greater than 1 to 100 ng (as sulfur). Sample size can be adjusted to provide an effective detection range from ~0.1-2500 vppm. Multiple analyses may be required if components are present at both sensitivity extremes.

QA/QC: The linear range of the detector must be defined through analysis of standards prior to sample analysis. Detector stability should be verified by frequent analysis of reference standards. Sample stability should be assayed for each matrix or samples analyzed immediately. Use of permeation standards will require that flow calibrations be performed. Duplicate analyses are recommended.

SAMPLING REQUIREMENTS: Applicable to moisture and particle free (S-04, S-06) grab or continuous samples (S-13).

EXTERNAL COST:

Per single analysis	\$50-\$200

INTERNAL COST:

Manhours/analysis	0.5-2

Capital Equipment:

Non-continuous gas chromatograph, temperature programmable, flame photometric detector	\$9,000-16,000

REFERENCES: Title 40, Code of Federal Regulations, Part 60, Appendix A 1980. [Method 15 - Determination of Hydrogen Sulfide, Carbonyl Sulfide, and Carbon Disulfide Emissions from Stationary Sources].

Lentzen, D. D., D. E. Wagoner, E. D. Estes and W. F. Gutknecht. EPA/IERL-RTP Procedures Manual: Level 1 Environmental Assessment. EPA-600/7-78-201, RTP, NC, January 1979. [NTIS No. PB 293795/AS].

METHOD NUMBER: A-01

ALTERNATE REFERENCES: Title 40, Code of Federal Regulations, Part 60, Appendix A, 1980. [Method 2 - Determination of Stack Gas Velocity and Volumetric Flow Rate (Type S Pitot Tube), Method 5 - Determination of Particulate Emissions from Stationary Sources, Method 6 - Determination of Sulfur Dioxide Emissions from Stationary Sources, Method 11 - Determination of Hydrogen Sulfide Content of Fuel Gas Streams in Petroleum Refineries, and Method 16 - Semicontinuous Determination of Sulfur Emissions from Stationary Sources].

METHOD NUMBER: A-02

ANALYTICAL METHOD: Gas Chromatography - Flame Ionization Detection, Vapor Phase Samples

ANALYTES: C_1 to C_{10} vapor phase hydrocarbons.

DESCRIPTION: Direct injection gas chromatography generally using porous polymer, carbon, or methyl silicone-coated packed or capillary columns. Temperature programming normally required for component resolution. Cryogenic trapping allows for sample concentration.

APPLICATIONS: Generally concentrations from 1 v% to 1 vppm may be analyzed directly by adjusting injection volume.

PREPARATIVE REQUIREMENTS: Sample should not contain particles, aerosols or condensates (S-04, S-06). High concentrations of vapor phase moisture may have deleterious effects on the analytical column.

LIMITATIONS: Multiple analyses may be required for accurate quantification of high and low concentration ranges within a single sample. Cyanide interferes with the analysis of C_2-C_3 hydrocarbons in some specific procedures. CO interferes with CH_4 in some procedures. Sample integrity is a concern if condensable quantities of C_4-C_{10} compounds present. Speciation of every potential isomer generally not attainable.

QA/QC: In addition to recommended laboratory practice, calibration checks and reference mixture analysis, condensation of less volatile components must be avoided or assessed.

SAMPLING REQUIREMENTS: Grab (S-13) or continuous samples may be analyzed.

EXTERNAL COST:

Per single analysis	\$50-\$100

INTERNAL COST:

Manhours/analysis	0.5-1

Capital Equipment:

Non-continuous gas chromatograph, temperature programmable with flame ionization detector	$10-12,000

PRIMARY REFERENCES: D. E. Lentzen, D. E. Wagoner, E. D. Estes and W. F. Gutknecht, "IERL-RTP Procedures Manual: Level I Environmental Assessment," (Second Edition), EPA-600/7-78-201, January 1979.

ALTERNATE REFERENCES: American Society for Testing and Materials. Annual Book of ASTM Standards. Philadelphia, PA, 1977. [Method DD3416-75T].

Title 40, Code of Federal Regulations, Part 60, Appendix A, 1980. [Method 25 - Addendum I. System Components].

USEPA. Proposed Rules. Federal Register, 45(77):26677-26682, April 1980. [Method 110 - Determination of Benzene from Stationary Sources].

Byron Hydrocarbon Analyzer or Equivalent (continuous monitor, methane/nonmethane).

METHOD NUMBER: A-03

ANALYTICAL METHOD: Gas Chromatography - Thermal Conductivity Detection, Vapor Phase Samples

ANALYTES: O_2, H_2, N_2, CO, CO_2, CH_4, H_2S

DESCRIPTION: Direct injection GC. Columns generally non-coated porous polymers and/or molecular sieves.

APPLICATIONS: Applicable for major gas species analysis at 0.5-100 v%.

PREPARATIVE REQUIREMENTS: Sample should not contain particles, aerosols, condensates (S-06). Vapor phase moisture generally unacceptable (S-04).

LIMITATIONS: H_2S (>0.5-1%) is an interference with some specific protocols. NH_3 (>0.5-1%) is an interference with some specific protocols. Argon usually not resolved from O_2. Sample stability is not a general concern if preparative requirements achieved.

SENSITIVITY: Usually ≥0.1-0.05% for all species except H_2 (MDL ∼5% unless platinum furnace detection) and $CH_4 \leq$ 0.5-1%.

QA/QC: Good laboratory practice including daily calibration verification and reference sample analyses usually sufficient. Duplicate determinations recommended.

SAMPLING REQUIREMENTS: Technique applicable for moisture and particle free (S-04, S-06) grab or continuous samples (S-13).

EXTERNAL COST:

Per single analysis	\$30-\$60

METHOD NUMBER: A-03

INTERNAL COST:

Manhours/analysis 0.5-1

Capital Equipment:

Non-continuous gas chromatograph with thermal conductivity detector	$4,000-$12,000

REFERENCES: Lentzen, D. D., D. E. Wagoner, E. D. Estes and W. F. Gutknecht. EPA/IERL-RTP Procedures Manual: Level 1 Environmental Assessment, EPA-600/7-78-201, RTP, NC, January 1979. [NTIS No. PB 293795/AS].

ALTERNATE REFERENCE: Title 40, Code of Federal Regulations, Part 60, Appendix A, 1980. [Method 3 - Gas Analysis for Carbon Dioxide Oxygen, Excess Air, and Dry Molecular Weight; Method 10 - Determination of Carbon Monoxide Emissions from Stationary Sources; and Method 11 - Determination of Hydrogen Sulfide Content of Fuel Gas Streams in Petroleum Refineries].

METHOD NUMBER: A-04

ANALYTICAL METHOD: Proximate Analysis of Solid Samples

ANALYTES: Moisture, volatile matter, ash, fixed carbon

DESCRIPTION: Moisture is determined from weight loss under controlled heating conditions; ash is determined by residue weight after burning. Volatile matter is determined by weight loss corrected for moisture. The fixed carbon is a calculated value resulting from the summation of percentages of moisture, ash, and volatile matter subtracted from 100.

APPLICATIONS: This technique can be applied to all solid wastes; the results for ashes and slags may not be as useful as proximate analyses of other solid wastes. Moisture determination coupled with ultimate analysis (A-05) results for ashes and slags may provide more reliable information on those materials.

PREPARATIVE REQUIREMENTS: The sample should be representative of the waste, and it should be gathered in a glass bottle to maintain sample integrity of volatiles.

LIMITATIONS: Inhomogeneity in the waste can cause major variations in results.

SENSITIVITY: Acceptable Precision:

	Repeatability (%)	Reproducibility (%)
Moisture	5	0.5
Ash	5	1
Volatiles	1	2

QA/QC: Duplicates per batch should be performed. Heating program of muffle furnace should be checked regularly.

SAMPLING REQUIREMENTS: Technique is applicable for all types of random or composite samples (S-01). Each test requires about 1 gram of sample.

EXTERNAL COST:

Per single analysis $30-200

INTERNAL COST:

Manhours/analysis	3-4

Capital Equipment:

Muffle furnace	$1,000-$5,000
Analytical balance	$2,000-$5,000

PRIMARY REFERENCES: American Society for Testing and Materials. Annual Book of ASTM Standards, Part 25. Philadelphia, PA, 1975. [Methods D013, D346, D3173, D3174, D3176]

American Society for Testing and Materials, Philadelphia, PA, "Annual Book for ASTM Standards, Method D-1888-78, Part 31 (1979)

Kopp, J.F. and G.D. McKee, "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020 (March 1979). [NTIS No. PB 297686/AS]

American Society for Testing and Materials, Philadelphia, PA, "Annual Book of ASTM Standards," Method D-1888-78, Part 31 (1979)

METHOD NUMBER: A-05

ANALYTICAL METHOD: Ultimate Analysis of Solid Samples

ANALYTES: Carbon and hydrogen in gaseous combustion products; sulfur, nitrogen and ash in the whole material; and oxygen by difference.

DESCRIPTION: Carbon and hydrogen are determined by burning the sample in a closed system and fixing the products. Nitrogen is determined by the Kjeldahl-Gunning method in which the nitrogen is converted into ammonium salts, decomposed, distilled, and titrated. The sulfur can be determined by the Eschka method, bomb washing method, or high-temperature combustion.

APPLICATIONS: This technique can be applied to all solid wastes.

GENERAL METHOD PARAMETERS:

Preparative Requirements: Samples representative of the waste should be stored in glass bottles. Technique is applicable for all types of random or composite samples (S-01). Approximately 10 gms of sample are necessary for ultimate analysis.

Method:

	Reference	Measurement
Carbon	ASTM D-3178-73 (1979)	CO_2 and H_2O on combustion
Nitrogen	ASTM D-3179-73 (1979), E-258-67 (1977)	N_2 by Kjeldahl
Oxygen	ASTM D-3176-76 (1979)	Difference method
Sulfur	ASTM D-3177 (1975), D-129-64 (1978)	Sulfate titration

LIMITATIONS: The carbon values include carbon in carbonates and hydrogen in the moisture and water of hydration of silicates. A modified Kjeldahl method must be used for nitrogen determination in oily wastes. Analysis of high ash content materials often varies.

SENSITIVITY: Acceptable precision (% difference):

Sulfur	0.10
Carbon	0.3
Hydrogen	0.07
Nitrogen	0.05
Ash	0.5

QA/QC: Blanks, standards and matrix replicates should be analyzed with each sample set. The precision of the analysis should be reported.

EXTERNAL COST:

Per single analysis	\$100-\$250

INTERNAL COST:

Manhours/analysis	2-6

Capital Equipment:

Analytical balance	\$2,000-\$5,000
Kjeldahl distillation unit	\$200-\$500
Carbon/hydrogen train	\$1,000-\$3,000
Sulfur apparatus	\$2,000-\$10,000
Tube furnace	\$200-\$500
Muffle furnace	\$1,000-\$5,000
Automated C,H,O,N,S, analyzer	\$25,000-\$35,000

PRIMARY REFERENCE: American Society for Testing and Materials, Philadelphia, PA, "Annual Book of ASTM Standards," Methods for each element, as specified above.

METHOD NUMBER: A-06

ANALYTICAL METHOD: Measurement of Radioactivity in Solids

ANALYTES: Gross α, Gross β, Radium-226

DESCRIPTION: For gross alpha and beta, a pulverized sample is slurried onto a 47 mm filter, dried and counted for emissions with a gas proportional counter. For Ra-226, a solid sample is ashed, digested and then the solution is measured for Ra-226 using the methods for liquid samples.

APPLICATIONS: This technique should only be applied to streams expected to concentrate radioactivity. In most cases, this will apply to ashes.

GENERAL METHOD PARAMETER:

Preparative Requirements: The sample should be representative of the waste, and solids and liquids should not be separated. The technique is applicable for all types of random or composite samples (S-01). Approximately 300 g of sample is required for testing.

Method: The solid is ground to a fine powder with a mortar and pestle. Transfer a maximum of 100 mg fixed residue for alpha assay and 200 mg fixed residue for beta assay for each 20 cm^2 of counting pan area. The residue is distributed uniformly in the pan by dispersing the dry residue of known weight that is spread with acetone and a few drops of Lucite solution. This is oven-dried at 103°C to 105°C weighed and counted using an internal proportional counter or geiger counter.

LIMITATIONS: The minimum limit of concentration for gross alpha and gross beta depends on sample size, counting system characteristics, background, and counting time. Only a thickness of 5 mg/cm^2 can be deposited in the counting planchet; therefore, only the radioactivity associated with that sample size can be analyzed. Limitations of the Ra-226 method include analytical precision during ashing and loss during alkaline borate fusion and acid dissolution followed by $BaSO_4$ and $PBSO_4$ precipitation, and reprecipitation from EDTA.

SENSITIVITY: The sensitivity for measuring radioactivity in solids is very dependent on the sample size and counting system characteristics. Lower detection limits can be achieved by increasing counting time.

QA/QC: For absolute gross alpha and gross beta and Ra-226 measurements, the detectors must be calibrated to obtain the ratio of count rate to disintegration rate, appropriate standards used, and the appropriate corrections made for system characteristics, background, self-absorption due to water, and geometry and particle counting efficiencies.

EXTERNAL COST:

Gross α	Per single analysis	\$50-\$200
Gross β	Per single analysis	\$50-200
Ra-226	Per single analysis	\$75-\$150

INTERNAL COST:

Gross α	Manhours/analysis	∿1
Gross β	Manhours/analysis	∿1
Ra-226	Manhours/analysis	∿4

Capital Equipment:

Gas-flow proportional counting system	$5,000-$20,000
Scintillation detector system	$5,000-$20,000

PRIMARY REFERENCES: American Society for Testing and Materials. Annual Book of ASTM Standards, Part 26. Part 45. Philadelphia, PA, 1979.

Harley, J.H., N.A. Hallden, and I.M. Fisenne. Beta Scintillation Counting with Thin Plastic Phosphors. Nucleonics 20, 1961. p. 59.

Halden, N.A., and J.H. Harley. An Improved Alpha-Counting Technique, Analytical Chemistry, 32, 1960. p. 1861.

Nuclear Science Series, USAEC Report, NAS-NS-301 to NAS-NS-3111, 1960-1974.

METHOD NUMBER: A-07

ANALYTICAL METHOD: X-Ray Diffraction Spectrometry for Qualitative Identification of Crystalline Phases in Solid Samples.

DESCRIPTION: Ground, solid sample is exposed to an x-ray beam. The intensity and pattern of peaks at diffraction angles from the rotated sample are used to identify compounds by special arrangement of atoms within the crystalline structure, using Bragg's Law.

APPLICATIONS: This technique is applicable only to completely dry solids expected to be crystalline, i.e., ashes, slags, and dewatered inorganic sludges.

PREPARATIVE REQUIREMENTS: The sample should be representative of the waste and should not be preserved chemically. Samples must be ground to minus 400 μ. Random or composite samples (S-01) may be analyzed using this method. Approximately 1 g of sample is required for each analysis.

LIMITATIONS: If the sample contains large amounts of amorphous material, background interference will be high. If numerous crystalline phases are present, diffraction patterns will be too complex for unquestionnable identification.

SENSITIVITY: In highly crystalline materials containing mixtures of several compounds, XRD can be both quantitative and qualitative. If the sample is primarily amorphous, this technique is imprecise.

QA/QC: Standard alignment procedures for generator, goniometer, and detector should be performed regularly. Alpha-quartz standards should also be analyzed. If quantitative results are required, standard method of additions must be employed. Duplicates in each batch should also be determined.

METHOD NUMBER: A-07

EXTERNAL COST:

Per single analysis	$40-$500 (depending on diffraction pattern complexity)

INTERNAL COST:

Manhours/analysis	4-20 (depending on diffraction pattern complexity
Capital Equipment:	
XRD Unit	$20,000-$75,000
Grinder	$200-$6,000

PRIMARY REFERENCE: Azaroff, L.V., Elements of X-Ray Crystallography, McGraw-Hill, New York, 1968.

METHOD NUMBER: A-08

ANALYTICAL METHOD: Optical or Scanning Electron Microscopy (SEM) and Scanning EM plus Energy Dispersive Analysis of X-rays.

ANALYTES: Bulk elemental chemistry (XRF) and particle morphology or particle size distribution.

DESCRIPTION: Small sample of dry solid is covered with vacuum-evaporated metal on carbon film, allowing secondary emission when placed in SEM and targeted by electron beam. While CRT is used to view magnified surface characteristics or size, x-ray fluorescence emission can be used to identify bulk elemental composition of specific or bulk surface areas. Optical microscopy provides a similar morphology and size data with less magnification.

APPLICATIONS: This technique is applicable to only dry solids. It is not applicable to tars or sludges.

GENERAL METHOD PARAMETERS:

Preparative Requirements: The sample should be as representative as possible. Aggregates should be maintained if possible. No chemicals should be added to the sample when collected. Samples from vapor phase streams should be collected isokinetically (S-03) on Nucleapore or equivalent filter substrates. For solid emission streams, technique is applicable for all types of random or composite samples (S-01). Less than 1 gram of sample is necessary for bulk XRF analysis.

LIMITATIONS: Samples viewed are on microscopic level; therefore, inhomogeneity in the solid sample can lead to great variability. It is important that the specimen is prepared such that it is truly representative of the sample. Elements detected by the associated energy dispersive spectrometer range in atomic number from sodium to uranium.

SENSITIVITY: Elements present at 5% or greater in the bulk sample will produce discernable XRF emission for elemental identification. Magnification on most SEM instruments can go up to 50,000X.

QA/QC: XRF standards should be run to assure proper detection of emission spectrum. Alignment to prevent optical abberations in viewed images should be performed before each sample batch.

EXTERNAL COST:

Per single analysis	$100-$1,000

INTERNAL COST:

Manhours/analysis	1-4
Capital Equipment:	
Scanning Electron Microscope	$50,000-$200,000
Vacuum Evaporator	$1,000-$2,000

PRIMARY REFERENCE: Goldstein, H.I. and J. Yakowitz. Practical Scanning Electron Microscopy. Planum Press, New York, 1975.

METHOD NUMBER: A-09

ANALYTICAL METHOD: Direct Aqueous Injection Gas Chromatography

ANALYTES: Non-extractable, non-purgeable organic compounds in water, e.g., carboxylic acids, alcohols, polyols, and other low molecular weight, polar compounds.

DESCRIPTION: Aqueous sample is injected directly into a gas chromatographic system which has a water compatible GC column. A variety of GC detectors can be used including mass spectrometry.

APPLICATIONS: Aqueous solutions of organic analytes including impinger solutions and leachates. Not applicable for low sample concentrations.

LIMITATIONS: Effective detection limits may be larger than usually obtained since no extraction-concentration step is used. The water can be an interference depending on the analytical conditions.

SENSITIVITY: 1-200 ng on column (1-50 mg/L sample). Sensitivity varies with analytes, sample matrix, and instrument.

SAMPLING REQUIREMENTS: Only 1-5 µL are commonly used for analyses. General practice would be to obtain a 5-20 mL sample in a glass vial. The sample should not contain suspended solids or oils. General organic sample handling practices should be followed.

EXTERNAL COST:

Per single analysis	\$25-\$300	(depending on matrix and GC detection technique employed)

METHOD NUMBER: A-09

INTERNAL COST:

Man-hours/analysis	1-3 (depending on matrix and GC detection technique employed)
Capital Equipment:	
Gas Chromatograph/ Mass Spectrometer	$90,000-$300,000
Gas Chromatograph with variety of alternate detectors	$5,000-$20,000

PRIMARY REFERENCES: DiCorcia, A. and R. Samperi, "Gas Chromatographic Determination of Glycols at the Parts-Per-Million Level in Water by Graphitized Carbon Black," Anal. Chem., 51 776-778 (1979)

Harris, L.E., W.L. Budde, and J.W. Eichelleyer. Analytical Chemistry, Vo. 46, No. 13, pp. 1912-1917, 1974.

METHOD NUMBER: A-10

ANALYTICAL METHOD: Gas Chromatography - Nitrogen Specific Detection

ANALYTES: Nitrogen containing organic compounds, such as amines, nitriles, isocyanates, heterocyclic nitrogen compounds (e.g., pyridines, carbazoles, quinolines)

DESCRIPTION: The sample or extract is injected onto a gas chromatographic column interfaced to a nitrogen/phosphorus specific detector (NPD), or a Hall electrolytic conductivity detector (HECD/N) in the nitrogen specific mode. Organic species which elute from the GC column are detected and a chromatogram obtained. The chromatogram is used to (1) determine if any nitrogen containing organic species are present (screening); (2) obtain an estimate of the total chromatographable nitrogen loading (total species method); or (3) determine the presence or concentration of selected compounds by comparison to an analytical standard.

APPLICATIONS: Generally applicable to all types of sample extracts containing nitrogen compounds.

GENERAL METHOD PARAMETERS:

Preparative Requirements: The sample is introduced by thermal desorption (P-03) or as an extract (P-01). Cleanup procedures, such as column separation (P-05) or solvent partitioning (P-04), are used particularly for complex samples as they remove interferences providing for more reliable identification and quantification of species present.

Total Species Methods: Nitrogenous organics are analyzed within a boiling point range of 50°C to 400°C. Nitrogenous organics are used for qualitative retention time and for quantitative detector response calibration.

Specific Organics: Specific nitrogenous organics are analyzed using the procedure given above or in the references. GC conditions are determined from the analysis of calibration standards containing the analytes of interest.

LIMITATIONS: The analytes must be chromatographable. High concentrations of other organics can interfere with the analysis. Solvents, such as hexane, pentane, or iso-octane, compatible with the detector are used. The detector stability is established and verified prior to sample analysis.

SENSITIVITY: 10-100 ng of each component tested.

QA/QC: Calibration standard solutions containing the component(s) of concern must be prepared and analyzed to generate a calibration curve. Blanks, calibration standards and matrix replicates should be analyzed along with every sample set. In the case where the sample complexity is sufficiently low to permit the use of GC/NPD for the determination of specific compounds, blank spikes, and matrix spikes should also be prepared and analyzed. The recovery and precision of the analysis should be reported.

EXTERNAL COST:

Per single analysis	$50-$200 (depending on qualitative or quantitative application and sample matrix)

METHOD NUMBER: A-10

INTERNAL COST:

Man-hours/analysis	1-6 (depending on qualitative or quantitative application and sample matrix)
Capital Equipment:	
Gas chromatograph with nitrogen/phosphorus or Hall Electrolytic conductivity detector	$12,000-$17,000

REFERENCES: USEPA. Proposed Rules. Federal Register, 44(233):69496-69500, December 6, 1979. [Method 607 - Nitrosamines]

Thrun, K.E., J.C. Harris, C.E. Rechsteiner, D.J. Sorlin, USEPA/IERL-RTP, "Methods for Level 2 Analysis by Organic Compound Category," EPA-600/57-81-029, July 1981

METHOD NUMBER: A-11

ANALYTICAL METHOD: Gas Chromatography - Mass Spectrometric Detection (GC-MS)

ANALYTES: Virtually any organic species which can be chromatographed including the following categories of organics of interest to synfuel effluents: aliphatics, aromatics, polynuclear aromatics, oxygenates (e.g., alcohols, ketones, phenols), nitrogenous and sulfur containing organics.

DESCRIPTION: The sample or sample extract is introduced into the GC/MS system. The organic species are separated by GC and a mass spectrum of each compound obtained. A computerized data system is typically used to acquire the data. Various computer programs can then normally be used to (1) identify compound by comparison to reference standards, (2) identify unknowns by comparison against computerized libraries, or (3) determine the concentration of the identified species. Unknown or unusual compounds may require manual interpretation.

APPLICATIONS: This method is best suited for providing a broad base of data concerning the composition and concentration of organics in waste samples, where this data is lacking. This method also provides reliable data concerning identification of compounds in support of other techniques, e.g., GC/FID.

GENERAL METHOD PARAMETERS:

Preparative Requirements: Samples can be introduced by thermal desorption (P-03) or as an extract [solvent extraction (P-01)]. Cleanup procedures such as column chromatography (P-05) and solvent partitioning (P-04) are useful for complex samples as they provide for more reliable identification and quantification by removal of interferences.

Method: For a survey analysis, the GC/MS is operated in the full mass range scanning mode with electron impact ionization. The extract (Method P-04), with or without additional cleanup procedures (Method P-05) of the semivolatile fraction of the sample or the sorbent trap (P-03), is spiked with an internal standard, such as phenanthrene-d_{10}. The total ion chromatogram for the sample is examined for the 20 most intense peaks, or for all peaks with an intensity of more than 1% of the total ion intensity (after eliminating background due to the GC column). Qualitative identification is attempted for all of the designated peaks by either computerized library searching or manual spectral interpretation.

Detection Limit

5 -20 ng of each compound, injected on-column

Other procedures are given in the references.

LIMITATIONS: Quantitative data is generally not as precise as that from conventional GC detection techniques. Low molecular weight compounds (MW <45) or compounds which have only low mass fragments can be difficult to measure due to the air background. Analysis of specific organics may be achieved using Method A-15.

SENSITIVITY: 1-100 ng per component on column.

QA/QC: The instrument is tuned routinely, e.g., DFTPP. Surrogates are typically added to the sample before preparation, in order to assess the overall method recovery and precision. Calibration solutions containing the analyte(s) of concern (if known), the surrogates and the internal standards are prepared and analyzed to generate a calibration curve. Blanks, calibration standards and matrix replicates should be analyzed with each sample set. The recovery of surrogates and precision of the analysis should be reported.

EXTERNAL COST:

Per single analysis	\$500-\$1200 (depending on sample complexity and necessity of manual interpretation)

INTERNAL COST:

Man-hours/analysis	2-20 (depending on sample complexity and necessity of manual interpretation)

Capital Equipment:

Gas chromatograph/mass spectrometer	\$90,000-\$400,000

PRIMARY REFERENCES: USEPA, Office of Solid Waste and Emergency Response. Test Methods for Evaluating Solid Waste Physical/Chemical Methods. SW-846. Washington, D.C., 1982.

USEPA. Proposed Rules. Federal Register, 44 (233):69464-69575, December 3, 1979. [Method 624 - Purgeables; Method 625 - Base/Neutrals, Acids and Pesticides]

Arthur D. Little, Inc. Sampling and Analysis Methods for Hazardous Waste Combustion. EPA Contract 68-0311, USEPA, February 1983

Keith, L.H., ed. Identification and Analysis of Organic Pollutants in Water. Ann Arbor Science, Ann Arbor, MI, 1977

Keith, L.H., ed. Advances in the Identification and Analysis of Organic Pollutants in Water. Ann Arbor Science, Ann Arbor, MI, 1981

METHOD NUMBER: A-12

ANALYTICAL METHOD: Gas Chromatography-Flame Ionization Detection (GC-FID)

ANALYTES: Virtually any organic species which can be chromatographed including aliphatics, aromatics, phenols, PNAs, etc. Formaldehyde and formic acid are the notable exceptions.

DESCRIPTION: The sample or sample extract is introduced into a gas chromatograph having a FID. Organic species which elute from the GC column are detected and a record (chromatogram) obtained. The chromatogram can be used to 1) determine if any organic species are present, (screening) 2) obtain an estimation of the total chromatographable organic loading (TCO), or 3) determine the presence or concentration of selected compounds by comparison to an analytical standard. A variety of GC columns are used. In general, these columns separate oganics by boiling point, or polarity. Both packed and capillary columns may be used.

APPLICATIONS: Applicable to gas samples collected on sorbents or in impinger solutions, as well as aqueous and solid samples. This method is well suited for long term monitoring of streams with a relatively consistent composition. The application of the method and the interpretation of data are relatively easy as compared to other techniques such as GC-MS, (A-11). The ease of application, when combined with the relatively low capital equipment cost, results in a broad range of analytical utilization and capability.

PREPARATIVE REQUIREMENTS: Numerous preparative methods for organics, previously described, are routinely employed [thermal desorption (P-03) and solvent extration, (P-01) etc.]. The column separation (P-05), solvent partitioning (P-04) and derivitization (P-02) methods are particularly useful for complex samples as they provide for more reliable identification and quantitation by removal of interferences.

LIMITATIONS: Method is not specific for any compounds. Identification is based on retention time only. This method cannot be used to unequivocally identify unknowns or provide any specific information about the unknown except estimated boiling point.

SENSITIVITY: 1-100 ng per component injected.

QA/QC: Analyst must run adequate controls and generally use good lab practices. Analytical checks by alternate methods, e.g. GC-MS, is a recommended practice, especially if changes are observed.

EXTERNAL COST:

Per single analysis	\$20-\$150	(depending on sample complexity and level of quantification required)

INTERNAL COST:

Manhours/sample	1-4	(depending on sample complexity and (level of quantification required)

Capital Equipment:

Gas chromatograph, temperature programmable, with flame ionization detector	\$5,000-\$15,000

REFERENCES: Lentzen, D.D., D.E. Wagoner, E.D. Estes and W.F. Gutknecht. EPA/IERL-RTP Procedures Manual: Level 1 Environmental Assessment, EPA-600/7-78-201, RTP, NC, January, 1979. [NTIS No. PB 293795/AS].

USEPA. Proposed Rules. Federal Register, 44(233):69464-69575, December 3, 1979. [Method 603 - Acrolein-Acrylonitrile, Method 604 - Phenols, Method 606 - Phthalate Esters, Method 610 - Polynuclear Aromatic Hydrocarbons].

USEPA, Office of Solid Waste and Emergency Response. Test Methods for Evaluating Solid Waste--Physical/Chemical Methods. SW-846. Washington, D. C., July 1982.

METHOD NUMBER: A-13

ANALYTICAL METHOD: Gravimetric Estimation of Organic Content in Solvent Extracts.

ANALYTES: Virtually all organic species with boiling points greater than 250-300°C.

DESCRIPTION: An aliquot of the sample extract is evaporated at room temperature in a tared weighing dish and weighed to constant weight. The gravimetric estimate can be used to (1) determine if any organic species with boiling points greater than 250-300°C are present (screening), or (2) obtain an estimate of the organic gravimetric content (GRAV).

APPLICATIONS: Applicable to extracts from gas samples collected on sorbents or in impinger solutions, as well as aqueous and solid samples. This method is well suited for long-term monitoring of streams with a relatively consistent composition, particularly when in combination with the GC/FID (TCO) technique (see Method A-12). The ease of application, when combined with the low cost of analysis, provides a rapid estimation of the total organic content (BP greater than 250-300°C) of a sample.

GENERAL METHOD PARAMETERS:

Preparative Requirements: Solvent extracts of samples are used for GRAV estimation (see solvent extraction Method P-01). The column separation (P-05) method is particularly useful for complex samples as they provide for more reliable identification and quantification by removal of interferences.

An aliquot corresponding to one-tenth of the concentrated sample extract, prepared according to the procedures in Methods P-01 and P-06 of this manual, is taken for gravimetric analysis.

METHOD NUMBER: A-13

Method: The aliquot is transferred to a clean, tared aluminum weighing dish and evaporated in a desicator at room temperature to constant weight (± 0.1 mg). The GRAV results are reported as mg of GRAV range organics (BP >300°C) per mL of extract and also per L (kg) of waste.

LIMITATIONS: Limitations include specific components are not identified; volatile organics (typically with boiling points less than 250°C) are not identified (see Method A-12 for quantification of more volatile species); and a relatively large quantity of extractable material is needed for the analysis.

SENSITIVITY: Sensitivity varies with sample size. Requires about 1 mg or more of residue.

QA/QC: Blanks and at least one pair of matrix replicates should be analyzed along with each sample set. The precision of analysis should be reported.

EXTERNAL COST:

Per single analysis	$20-$40

INTERNAL COST:

Manhours/analysis	0.5-1
Capital Equipment:	
Analytical balance	$1,000-$3,000

METHOD NUMBER: A-13

PRIMARY REFERENCE: Lentzen, D.E., D.E. Wagoner, E.D. Estes and W.F. Gutknecht. EPA/IERL-RTP Procedures Manual: Level 1 Environmental Assessment, Second Edition. EPA-600/7-78-201, RTP, NC, October 1978. [NTIS No. PB 293795/AS]

METHOD NUMBER: A-14-A

ANALYTICAL METHOD: Estimation of Quantities of Categories of Organics by Infrared Analysis Total Species Method

ANALYTES: Aliphatics (including alkenes) and oxygenated organics (including alcohols, ketones, aldehydes, ethers, esters and carboxylic acids) have been chosen for class quantification by this method.

DESCRIPTION: Solution spectroscopy is a widely-accepted technique for quantitative analysis, as it provides a reproducible molecular environment. Correlations between vibrational frequencies and molecular structure are most valid when a material is examined in dilute solution in an inert, non-polar solvent.

Beer's law is applicable in the low concentration range of non-interacting solvents which makes infrared spectroscopy an ideal method for monitoring the concentration of known constituent in a stream.

APPLICATIONS: The time required for analysis is relatively short once the calibration curves are prepared. The technique can also provide reliable qualitative data about a sample containing few compounds at a low cost.

GENERAL METHOD PARAMETERS:

Preparative Requirements: An extract (P-01) of the solvent sample must be obtained before analysis. Solvent partitioning (P-04) or column separation (P-05) methods can be used to reduce the complexity of the spectra generated by this method.

METHOD NUMBER: A-14-A

Method Description: A general solution method with the procedure for quantification dependent on knowledge of the sample to be analyzed is described. The method is applied to monitor the concentration of a group of similar compounds, for instance n-alkanes. A calibration curve is prepared, using the specific organic compound identified for each general compound class, i.e., for alkyl ethers use butyl ether as a reference. If another alkyl ether is known to be present, then the calibration curve could be prepared using the known ether.

Table 14-A-1 lists analytes, solvents to use, analytical bands and reference compounds. One of two solvents has been suggested for each compound class, based on the frequencies chosen for analysis. Tetrachloroethylene is recommended for the 4000-1400 cm^{-1} range and hexane for the 1300-800 cm^{-1} range. These spectrophotometric solvents are virtually transparent in the chosen frequency ranges.

The calibration curve should be based on a minimum of three concentration levels, prepared on a weight-volume basis and examined in the same solution cell. The cell should be thoroughly cleaned with the solvent and the calibration solutions run in increasing concentration order.

The recommended cell path is 0.1 mm; for this cell path, 10% (10 grams per 100 cc) is the highest useful concentration. Therefore, 1%, 5%, and 10% concentrations are recommended. Prepare the calibration curve based on the starred (see Table 14A-1) peak maxima at each concentration level, using the specific organic recommended or the specific organic known to be present.

The ratio test should first be applied to test for interferences. The sample spectrum is recorded "neat", i.e., between KBr plates as a capillary film or in a KBr pellet of a solid. The absorbance intensities ratio of the two analytical bands is compared to the ratio obtained for the reference organic. If the ratios are more than 20% different, this indicates probably interferences and the infrared method should not be used. If less than 20% different, the total species concentration can be determined using this method.

The sample or sample extract is then weighed and dissolved in the same solvent at a concentration that is near the mid-point of the calibration range. Several dilutions may be necessary to reach the optimum 0.2-0.7 absorbance range. Record the spectrum using the same cell as for the calibration curve. Note whether the peak maxima are within 10 cm^{-1} of the maxima for the organic reference compound. If not this may also indicate interferences. Read the analyte concentration from the calibration curve, using the intensity at peak maximum and extrapolate the sample concentration before dilution.

LIMITATIONS: This method requires a skilled analyst for preparation of solutions and construction of calibration curves. Application of the ratio test may require judgment based on some experience. The analyte should be in as pure a state as possible, since the reliability of the information obtained decreases as the number of components increases. Presence of unexpected functionalities in the spectrum is considered a strong interference. The ratio test is an indication of interference by a similar functionality. For instance, carbonyl functionality is not unique to a particular category; thus presence of an ester may interfer with ketone quantification.

SENSITIVITY: 50 μg to several milligrams.

QA/QC: Calibration solutions are prepared and analyzed to generate a calibration curve. Spectroquality solvents should be used for solution preparation. The solvents should be examined in the cell for cleanliness. As noted in the Description Section, the cell should be thoroughly cleaned with the solvent and the calibration solution run in increasing concentration order. The baseline method for quantitative analysis, as described in Potts[2], should be used for peak intensity measurement. Parameters for the IR spectrophotometer should be optimized as recommended by the manufacturer.

TABLE 14A-1

Category	Analytes	Infrared Solvent	Analytical Bands	Reference Compound
Aliphatics	Alkanes	C_2Cl_4	*2920/1470	hexane
	Cycloalkanes	C_2Cl_4	*2920/1445	cyclohexane
	Alkenes	C_2Cl_4	3080/1650*	1-octene
	Alkadiene	C_2Cl_4	3040/1640*	1,7 - octadiene
Alcohols	Alkyl Alcohols	C_2Cl_4	*3350/1065	butanol
	Cycloalcohols	C_2Cl_4	*3350/1060	cyclohexanol
	Cellosolves	C_2Cl_4	*3420/1055	cellosolve
Ketones	Alkyl Ketones	C_2Cl_4	*1725/1170	2-pentanone
	Cycloketones	C_2Cl_4	*1695/1200	cyclooctanone
	Aromatic Ketones	C_2Cl_4	*1660/1275	benzophenone
Aldhydes	Alkyl Aldehydes	C_2Cl_4	2710/1725*	butyraldehyde
	Aromatic Aldehyde	C_2Cl_4	2715/1700*	benzaldehyde
Ethers	Alkyl Ethers	C_6H_{14}	2960/1120*	butyl ether
	Aromatic Ethers	C_6H_{14}	3015/1095*	benzyl ether
	Dioxanes	C_6H_{14}	2840/1120*	p dioxane
Esters	Alkyl Esters	C_2Cl_4	1740/1180*	ethyl butyrate
	Aromatic Esters	C_2Cl_4	1730/1275*	di-2-ethylhexyl phthalate
Carboxylic Acids	Alkyl Acids	C_2Cl_4	*1710/1275	acetic acid
	Aromatic Acids	C_2Cl_4	*1680/1285	benzoic acid

* The starred band absorbance intensity is to be used in preparing the calibration curve; both bands are used for the ratio test.

METHOD NUMBER: A-14-A

EXTERNAL COST:

Per single analysis	\$30-\$2,000 (depending on complexity of sample, spectroscopic technique and level of interpretation)

INTERNAL COST:

Manhours/analysis	1-40 (depending on complexity of sample, spectroscopic technique and level of interpretation)
Capital Equipment: IR spectrometer	\$10,000-\$20,000 (to \$100,000 for Fourier-Transform IR)

REFERENCES: Lentzen, D.E., D.E. Wagoner, E.D. Estes, and W.F. Cutknecht. EPA/IERL-RTP Procedures Manual: Level 1 Environmental Assessment, Second Edition, EPA-600/7/78-201, RTP, NC, October 1978 (NTIS No. PB 293795/A.S)

Potts, W.J., Jr., Chemical Infrared Spectroscopy, Vol. 1, Techniques, John Wiley and Sons, Inc. (1963)

Smith, A.L., Applied Infrared Spectroscopy, John Wiley and Sons (1979)

METHOD NUMBER: A-14-B

ANALYTICAL METHOD: Estimation of Quantities of Categories of Organics by Ultraviolet Spectroscopy.

ANALYTES: UV for category identification is useful for material with functionalities such as aromatics, conjugated unsaturation, and conjugated carbonyls.

DESCRIPTION: The ultraviolet region of the electromagnetic spectrum is usually divided into two regions, the vacuum UV and the quartz UV. The quartz UV region, from 200 to 400 mm, is used for analytical measurements which are based on electronic transitions in the analytes. Samples and sample extracts are dissolved in UV transparent solvent, the absorbance at a specific wavelength measured, and the concentration extrapolated. As in infrared, Beer's Law is applicable for low concentrations in non-interacting solvents allowing quantities of compound categories to be determined.

GENERAL METHOD PARAMETERS:

Preparative Requirements: An extract (P-01) of the sample is dissolved in a non-UV absorbing solvent. Solvent partitioning (P-04) or column separation (P-05) can be used to reduce the number of components.

Method Description: In order to quantify the amount of material in a sample, a calibration curve for the material is necessary. Three solutions of known concentrations of an analytical standard are made up and the absorption at a specific wavelength is measured. The absorption is plotted against concentration of the standards. The standards are usually run in a 1 cm path length quartz cell with a blank (cell and solvent) in the reference beam. The standards are run in ascending concentration order with ample washing of the cell between runs. The sample is then analyzed in the same cell, the absorbance at the recommended wavelength measured and the concentration determined from the calibration curve and extrapolated to an undiluted sample.

The analytical wavelength to be used for the analysis should be determined during the Phase I monitoring program by ascertaining a λmax for each sample type. Reference compounds for calibration curves can be chosen on the basis of a material most similar to those found in the stream of interest.

LIMITATIONS: Measurements can only be accurately made on samples containing components with large extinction coefficients (E max∿ 5000). Components with similar chromophoric groups (conjugated ketones and aldehydes) will overlap and may cause interference problems in the analysis.

SENSITIVITY: The expected sensitivity will vary with the extinction coefficient of the analytes and the cell path length. Typically, 10 μg to 100 mg can be determined.

QA/QC: Calibration solutions are prepared and analyzed to generate a calibration curve. Spectral quality solvents should be used for all analyses. This is particularly important if UV absorbances are low and solvents might cause interferences. Cells should be well cleaned and both cell blanks and solvent blanks should be run. Optimum instrument parameters, as specified by the instrument manufacturer should be used.

EXTERNAL COST:

Per single analysis	\$30-\$2,000

INTERNAL COST:

Manhours/analysis	2-3 (depending on complexity of sample, technique and level of interpretation)
Capital Equipment	$5,000 - $50,000 (depending on resolution and automation)

PRIMARY REFERENCES: Lentzen, D.E., D.E. Wagoner, E.D. Estes, W.F. Gulknecht. IERL-RTP Procedures Manual: Level 1 Environmental Assessment, Second Edition. EPA-600/7-78-201, EPA, RTP, NC, October 1978, (NTIS No. PB 293795/AS).

Bauman, R.P., Absorption Spectroscopy. John Wiley, New York, 1962.

METHOD NUMBER: A-14-C

ANALYTICAL METHOD: Category Identification of Organics by Low Resolution Mass Spectrometry.

ANALYTES: All chemical classes may be determined by Low Resolution Mass Spectrometry (LRMS). In a complex mixutre, clean-up of the sample may be helpful.

DESCRIPTION: LRMS plays an important role in the determination of the chemical composition of organic mixtures. By this method, one can identify a chemical class and give an order of magnitude quantitation. Complimentary information available from liquid chromatographic separations (Method Number P-05) and from interpretation of infrared spectra of the mixture may be useful for interpretation.

APPLICATIONS: The technique can be used for qualitative identification of various species. Interpretation of complex spectra may be difficult and time consuming. The analysis results obtained by LRMS are reported primarily as chemical classes and molecular weight ranges of those classes, with subcategory or specific compound or composition designation whenever possible.

GENERAL METHOD PARAMETERS:

Preparative Requirements: An extract (Method P-01) of the sample is usually analyzed. Solvent partitioning (P-04) or column separation (P-05) can be used to reduce the complexity of the spectra.

Method Description: The detail that may be obtained from the mass spectrum of multicomponent mixtures is dependent both on the complexity of the spectrum itself, and on the amount of supplemental information that is available. The precision of the identification that may be obtained will vary accordingly, ranging from specific compound or composition assignments for all of the spectrum, to simply an indication of the chemical classes that are present. The task confronting the analyst of the mass spectra of multicomponent mixtures is to discover the correct combination of individual spectra that will adequately account for the experimentally observed spectrum. The additive nature of superimposed mass spectra assures that this is possible, and the multi-peak nature of electron impact mass spectra makes it practical in most cases. The combination of the two aspects ensures that if the observed mass spectrum is fully accounted for by the combined individual assignments, than those assignments are an accurate indication of the chemical class makeup of the sample.

Two principal techniques are used to provide clues to the analyst for tentative individual chemical class or compound assignments. The first and most important of these is the fractional distillation of the sample that occurs as the direct insertion probe is slowly taken through its complete temperature cycle from cool to hot. The second is the use of both high (70 eV electron impact), and low (10 to 20 eV) electron impact or chemical ionization modes, at or near the same probe temperature.

The thermal distillation provides a separation into successive molecular weight ranges, and the change of ionization mode differentiates between parent and fragment ions. All of the data, taken in combination, provides enough information for overall spectral interpretation.

Tentative assignments, made on the basis of the above information, are confirmed or modified in the confirmation phase of the analysis.

In the confirmatory phase, standard spectra obtained either from the literature, or from reference compounds are used to evaluate how completely the experimentally observed mass spectrum is accounted for by the combined tentative individual assignments.

Several interpretation aids can be helpful in the analysis of the LRMS data. The first of these is a table of mass numbers and associated Z values, where the Z value is given by the relationship:

$$MW - C_nH_{(2n + Z)}$$

A Z value for any ion in the spectrum can be correlated with a limited range of possible chemical classes, and a very limited range of possible chemical compositions. Mass values for PAH species can be correlated to specific chemical compositions and numbers of rings, although not to specific isomers. In most cases, similarly specific chemical composition assignments can be made to individual mass values for aza-arenes, and for oxygen or sulfur containing polycyclic species.

LIMITATIONS: The complexity of a sample and the time necessary for interpretation are severe limitations to the technique. The reliability of the information obtained decreases as the complexity of the sample increases.

SENSITIVITY: 50 ng to 10 μg depending on matrix and sample type.

QA/QC: Since the technique is very sensitive, care should be taken not to introduce contamination during the preparation steps. To account for contamination, field and method blanks should be analyzed with each sample set.

METHOD NUMBER: A-14-C

EXTERNAL COST:

Per single analysis	$100-$2,000 (depending on complexity of sample and level of interpretation)

INTERNAL COST:

Manhours/analysis	1-40 (depending on complexity of sample and level of interpretation)
Capital Equipment Mass Spectrometer	$90,00-$400,000(depending on resolution and automation)

PRIMARY REFERENCES: Lentzen, D.E., D.E. Wagoner, E.D. Ester, and W.F. Gutknecht. IERL-RTP Procedures Manual: Level 1 Environmental Assessment, Second Edition. EPA-600/7-78-201, EPA, RTP, NC, October 1978, [NTIS No. PB 293795/AS].

"Eight Peak Index of Mass Spectra", 4 volumes, 2nd edition, published by Mass Spectrometry Data Centre, AWRE, Aldermaston, Reading, RG7 4PR, United Kingdom, 1974

Heller, S.R.; and Milne, G.W.A., "EPA/NIH Mass Spectral Data Base", 5 volumes, U.S. Department of Commerce/National Bureau of Standards, NSRDS-NBS 63, December 1978.

Stauffer, J., "Interpretation of Low Resolution Mass Spectra for Level 1 Analysis of Environmental Mixtures" Report prepared for US EPA/IERL, N.C., Contract No. 68-02-311, September 1980.

METHOD NUMBER: A-15

ANALYTICAL METHOD: Specific Compound Monitoring by GC/MS

ANALYTES: Virtually any organic species which can be chromatographed including the following categories of organics of interest to synfuel effluents: aliphatics, aromatics, polynuclear aromatics, oxygenates (e.g., alcohols, ketones, phenols), nitrogenous and sulfur containing organics.

DESCRIPTION: The GC/MS system is operated in a selective mode (commonly termed SIM or MID) which allows better sensitivity and specificity for selected compounds. The analytical sensitivity and specificity are improved by increasing the dwell time on characteristic ions (representative of key fragments) of the compound. This procedure is similar to method A-11, however, it is directed towards the analysis of specific organic(s).

APPLICATIONS: This technique is generally used for 1) measuring low levels of compounds expected to be present or 2) measuring specific compounds in the presence of high concentrations of other components.

GENERAL METHOD PARAMETERS:

Preparative Requirements: Samples may be prepared for analysis by virtually any of the preparative techniques described (solvent extraction (P-01), derivatization (P-02), thermal desorption (P-03), solvent partitioning (P-04), column clean up (P-05), or microextraction (P-06)). Extensive clean-up techniques are usually not necessary because of the specificity of the method.

Method: For the analysis of specific organics, the GC/MS is operated in the selected ion monitoring mode with electron impact ionization.

An internal standard, such as phenanthrene-d_{10} is added to the sample, as a retention time marker and may also be used to determine relative responses for quantification. Typical GC/MS conditions for volatile and semi-volatile organics are given in Method A-11.

LIMITATIONS: Within a sample the technique is generally limited to a small group (<20) of compounds such as PNAs. Identification of species is often not as reliable as full scan GC/MS. Mass spectral data for identification of other organic species is not obtained during specific compound monitoring.

SENSITIVITY: 5-20 ng of each compound injected on column (50 ng for mixtures like PCBs).

QA/QC: The instrument is tuned routinely, e.g., DFTPP. Surrogates are typically added to the sample before preparation, in order to assess the overall method recovery and precision. Calibration solution(s) containing the analytes of concern, the surrogates and the internal standard are prepared and analyzed to generate a calibration curve. Blanks, calibration standards, blank spikes, matrix spikes and matrix replicates should be analyzed with each sample set. The recovery and precision of the analysis should be reported.

EXTERNAL COST:

Per single analysis	\$200-\$1,000

INTERNAL COST:

Manhours/analysis	2-4

Capital Equipment:

Gas chromatograph/mass spectrometer	\$90,000-\$400,000

PRIMARY REFERENCES: Radian Corporation, Assessment, Selection and Development of Procedures for Determining the Environmental Acceptability of Synthetic Fuel Plants Based on Coal. Austin, TX, May 1977. [NTIS FE-1795-3]

U.S. Environmental Protection Agency/Office of Solid Waste, Washington, DC, "Test Methods for Evaluating Solid Waste Physical/Chemical Methods," SW-846 (1980)

U.S. Environmental Protection Agency, Federal Register, 44, 69464-69575 (December 3, 1979)

METHOD NUMBER: A-16

ANALYTICAL METHOD: High Pressure Liquid Chromatography (HPLC)

ANALYTES: Various polar, non-volatile or heat labile analytes such as PNAs, phenols, alcohols and carboxylic acids.

DESCRIPTION: The sample extract and/or aqueous and organic (effluent) samples are injected onto a high performance liquid chromatographic column. Eluting analytes are detected and measured by detectors relying on UV abosrbance, fluroescence, electrochemical oxidation or refractive index. This method can sometimes provide specific identification of isomers which cannot be resolved by gas chromatography. The choice of column and solvent system is dependent upon the particular species being analyzed.

APPLICATIONS: This analysis method is applicable to aqueous samples and extracts from all types of samples. Detector selection is based both on the sensitivity required and the compounds analyzed as shown in Table A-2.

GENERAL METHOD PARAMETERS:

Preparative Requirements: Sample must be in solution in a non-interferring solvent. Sample may require column cleanup (P-05), solvent partitioning (P-04), or derivitization techniques (P-02) to remove interferences.

Method: Generally, a HPLC method using a reversed-phase C_{18} column is applicable for analyzing a number of categories of organics, including polynuclear aromatics, phenols, carboxylic acids, nitrocresols, nitrogen containing organics and aldehydes. The analytes are typically eluted from the column using a water/acetonitrile (or methanol) solvent system. For carboxylic acids and some phenols, it is necessary to add acetic acid to the solvent system. For aldehydes, the organics are reacted to form Dinitrophenyl Hydrazine (DNPH) derivatives (Method P-02).

TABLE A-2. HPLC DETECTOR CHARACTERISTICS

Detector	Principle	Approx. Sensitivity	Applications	Limitations	Approx. Cost
UV Absorbance					
Fixed λ	Analyte detected by its UV absorbtion in non-absorbing mobile phase. UV wavelength is fixed.	10^{-7}-10^{-6} g analyte injected for strong UV absorbers	Compounds showing UV absorbance at fixed wavelength of instrument measurement usually 254 µm (PNAs)	Response factors may vary widely. Mobile phase must be UV transparent.	$3,000
Variable λ	UV wavelength available through use of a prism or gravity monachromator.	10^{-7}-10^{-6} g analyte injected	Compounds having UV absorbance at any wavelength e.g., 200-400 µm (PNAs, phenols, aromatics)	Response factors vary widely. Mobile phase must be UV transparent.	$5-10,000
Fluorescence	Analytes detected by light emitted (fluorescence) when irradiated with UV light.	10^{-9}-10^{-6} g analyte injected	Compounds which fluoresce or can be induced to fluoresce e.g., indoles, PNAs, etc. Relatively specific.	Fluorescence may be inhibited by various conditions. Compound specific, narrow linear range.	$10-20,000
Electrochemical	Analyte is oxidized or reduced at electrode. Current (i) is measured in microamps.	10^{-12}-10^{-9} g analyte injected	Phenols, amines, catechols, and other easily oxidized or reduced species.	Compound specific, narrow linear range. Requires polar mobile phase.	$2-5,000
Differential Refractometer	Analytes detected by their refractive index in solution.	10^{-5}-10^{-6} g analyte injected	Most general detector available. Potentially applicable to all species of compounds, low specificity.	Low sensitivity. Cannot vary mobile phase composition.	$3-5,000

Polynuclear aromatics and aldehydes are two categories or organics expected to be present in synfuel effluents. The HPLC techniques described below for these two categories, are highly specific and, therefore, are recommended particularly for monitoring.

Sensitivity: 0.1 ng to 100 ng each PNA on column. 5 to 20 ng each aldehyde on column.

LIMITATIONS: Often less sensitive than GC methods, but more specific. Detector response varies widely for different analytes. Requires use of standards for quantitation and identification. Some analytes may require derivatization. Unequivocal compound identification is not usually achieved.

SENSITIVITY: Varies widely with nature of analyte and detectors. Approximately 10 ng to 10 μg of injected components.

EXTERNAL COST:

Per single analysis	\$75-\$200 (depending on sample matrix and degree of quantitation)

INTERNAL COST:

Manhours/analysis	1-3 (depending on sample matrix and degree of quantitation)
Capital Equipment:	
High Performance Liquid Chromatograph	\$15,000-\$50,000

METHOD NUMBER: A-16

PRIMARY REFERENCES: Dillon, H.K., R.H. James, H.C. Miller, and A.K. Wensky (Battelle Columbus Laboratories, Columbus, Ohio). POHC Sampling and Analysis Methods. Contract No. 68-02-2685, Report prepared by Southern Research Institute, Birmingham, AL, USEPA/IERL, RTP, NC, December 1981

Kuwata, K., M. Uebori, and Y. Yamasaki. Determination of Aliphatic and Aromatic Aldehydes in Polluted Airs as Their 2,4-Dinitrophenylhydrazones by High Performance Liquid Chromatography. J. Chromatogr. Sci., 17, 1979, pp. 264-268

US EPA. Proposed Rules. Federal Register, 44(233):69514-69517, December 3, 1979. [Method 610 - Polynuclear Aromatic Hydrocarbons]

METHOD NUMBER: A-17

ANALYTICAL METHOD: Total Organic Halogen Determination (TOX)

ANALYTES: Halogenated Organics (nonspecific)

DESCRIPTION: Halogenated organics are combusted and analyzed in a microcoulometric titration cell.

APPLICATION: Aqueous samples

GENERAL METHOD PARAMETERS:

Preparative Requirements: Samples are kept cool (4°C). Grab (S-11) or composite (S-10) aqueous samples are analyzed using this method.

Method: Halogenated organic compounds are sorbed on activated carbon. The carbon is rinsed with nitric acid to remove inorganic halide components. The micro carbon plug is placed in a combustion furnace and organohalide compounds converted to gaseous acid halides which are swept into a microcoulometric titration cell. The halides are titrated with a standard silver nitrate solution.

LIMITATIONS: Samples with high inorganic halide levels (brines, seawater) will result in positive interference due to incomplete inorganic halide removal.

SENSITIVITY: 5-100 µg/L.

QA/QC: Calibration solutions are prepared and analyzed to generate a calibration curve. Blanks, calibration standards, blank spikes, matrix spikes and matrix replicates should be analyzed with each sample set. The precision and recovery of analysis should be reported. Carbon columns in series may be analyzed in order to check for halogenated organic breakthrough.

METHOD NUMBER: A-17

EXTERNAL COST:

Per single analysis	\$25-\$100

INTERNAL COST:

Manhours/analysis	1-3
Capital Equipment:	
TOX analyzer	\$10,000-\$20,000

REFERENCE: US EPA. Office of Research and Development, EMSL, Physical and Chemical Methods Branch. Total Organic Halide, Interagency Method 450.1. Cincinnati, OH. November 1980

Kopp, J.F. and G.D. McKee, "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020 (March 1979). NTIS No. PB297585/AS

METHOD NUMBER: A-18

ANALYTICAL METHOD: Gas Chromatography - Sulfur Specific Detection

ANALYTES: Sulfur containing organic compounds: e.g., thiophenes, benzothiophenes, etc.

DESCRIPTION: Sample or sample extract is injected into a gas chromatograph equipped with a flame photometric detector (FPD) or a Hall electrolytic conductivity detector configured in the sulfur mode (HECD-S). Either the detector is specific for sulfur containing compounds.

APPLICATIONS: Method can be used to screen samples for sulfur compounds or to determine individual species.

PREPARATIVE REQUIREMENTS: Thermal desorption (P-03) or solvent extraction (P-01) methods are generally most appropriate.

LIMITATIONS: High concentrations of other organics can interfere. The stability of the detector is varible. Solvent must be detector compatible.

SENSITIVITY: 1-10 ng per component injected.

QA/QC: Frequent calibration, in addition to good general laboratory practices.

EXTERNAL COST:

Per single analysis	\$50-\$250 (depending on sample matrix and degree of quantification)

INTERNAL COST:

Manhours/analysis	1-6 (depending on sample matrix and degree of quantification)

Capital Equipment:

Gas chromatograph with either flame photometric or HECD(S) detector	$10,000-$17,000

REFERENCE: Keith, L.H., ed. Energy and Environmental Chemistry - Fossil Fuels. Ann Arbon Science, Ann Arborn, MI, 1982. 443 pp.

US EPA/IERL, RTP, "Methods for Level 2 Analysis by Organic Compound Category," EPA-600/57-81-029, July 1981.

METHOD NUMBER: A-19

ANALYTICAL METHOD: Gas Chromatography - Photoionization Detection

ANALYTES: Aromatic species such as benzene, toluene, naphthalenes, xylenes, anilines.

DESCRIPTION: Sample is injected or purged into gas chromatograph equipped with photoionization detector (PID). Aromatic compounds are selectively detected in presence of aliphatic hydrocarbons. Method can be used quantitatively or as a screening technique.

APPLICATIONS: Generally applicable to sample extracts and volatile species collected on sorbents.

PREPARATIVE REQUIREMENTS: Thermal desorption (P-03) and solvent extraction (P-01) are the most common preparative methods.

LIMITATIONS: Not applicable to compounds which have no ultraviolet chromophores. High concentrations of other organic species can interfere.

SENSITIVITY: 0.2 to 1 ng analyte injected.

QA/QC: Good laboratory practices and multipoint calibrations necessary for quantitation.

EXTERNAL COST:

Per single analysis	\$50-\$300 (depending on sample matrix and degree of quantitation)

INTERNAL COST:

Manhours/analysis	1-6 (depending on sample matrix and degree of quantitation)

Capital Equipment:

Gas chromatograph with photoionization detector	\$10,000-\$15,000

REFERENCES: USEPA. Proposed Rules. Federal Register, 44(233):69474-69478, December 3, 1979. [Method 602 - Purgeable Aromatics].

Cox, R. D., and R. F. Earp. Determination of Trace Level Organics in Ambient Air by High-Resolution Gas Chromatography with Simultaneous Photoionization and Flame Ionization Detection. Anal. Chem., 54(13):2265, 1982.

John H. Driscoll, et. al. The Photoionization Detector in Gas Chromatography, American Laboratory, 10, 1978. p. 137.

ANALYTICAL METHOD: pH Measurement

ANALYTES: H^+ ion concentration

DESCRIPTION: The pH is determined using a glass electrode.

APPLICATIONS: Aqueous samples.

GENERAL METHOD PARAMETERS:

Preparative Requirements: This analysis method is applicable to grab samples (S-11) and continuous sampling (S-10)

Method: The pH of the sample is determined electronically using either a glass electrode in combination with a reference potential or a combination electrode, as specified in SW-846.

LIMITATIONS: The sample pH may change with time, therefore, pH should be determined as soon as possible after collection. If not determined within 6 hours, the time of determination after collection shall be referenced.

SENSITIVITY: Depends upon pH meter - usually 0.01 to 0.1 pH units

QA/QC: Samples should be analyzed in duplicate. The pH meter and electrode(s) should be calibrated using aqueous buffers at a minimum of 2 pH levels; at least one calibration pH should be within 2 pH units of the sample value. Grab samples (S-11) or continuous sample (S-10).

EXTERNAL COST:

Per single analysis	\$5-\$15

METHOD NUMBER: A-20

INTERNAL COST:

Manhours/analysis	0.1-0.2
Capital Equipment:	
pH meter with electrodes	$300-$1,300

REFERENCES: US EPA. Proposed Rules Federal Register, 44 (233). December 3, 1979. [Amendment to 40 CFR 136]

American Society for Testing and Materials, Annual Book of ASTM Standards, Part 31. Philadelphia, PA, 1981. p. 178. [Method D-1293 - pH of Water and Wastewater] (1981)

American Public Health Association, American Water Works Association, and Water Pollution Control Federation. Standard Methods for the Evaluation of Water and Wastewater, 14th edition. APHA, Washington, D.C., 1976. p. 460, [Method 424 - pH Value].

U.S. Environmental Protection Agency/Office of Solid Waste, Washington, D.C., "Test Methods for Evaluating Solid Waste - Physical/Chemical Methods," SW-846 (1980), Section 5.

METHOD NUMBER: A-21

ANALYTICAL METHOD: Total Solids Measurement

ANALYTES: Total solids content

DESCRIPTION: Total solids in aqueous samples are determined gravimetrically.

APPLICATIONS: Aqueous samples.

GENERAL METHOD PARAMETERS:

Preparative Requirements: Samples are kept cool (4°C) to minimize biological decomposition of solids. Grab (S-11) or composite (S-10) samples may be analyzed using this method. Sample should be mixed to ensure a representative aliquot is taken.

Method: Total solids are determined by evaporation of moisture using a hot water bath and gravimetric determination of the solid residue remaining after equilibration at 105°C. Total volatile solids are determined by heating to 550°C.

LIMITATIONS: Inhomogeneity in the sample can cause major variations in results.

SENSITIVITY: Usually 0.1 to 0.5 mg can be weighed with accuracy.

QA/QC: Blanks and matrix replicates should be analyzed with each sample set. The precision of analysis should be reported.

EXTERNAL COST:

Per single analysis	\$5-\$15

METHOD NUMBER: A-21

INTERNAL COST:

Manhours/analysis	0.1-0.2
Capital Equipment:	
Oven, balance	$1,000-$3,000

REFERENCES: USEPA. Proposed Rules. Federal Rigister, 44(233), December 3, 1979. [Amendment to 40 CFR 132]

American Society for Testing and Materials, Annual Book of ASTM Standards, Part 31. Philadelphia, PA, 1981. [Method D-1888 - Tests for Particulate and Dissolved Matter in Water]

USEPA, Office of Technology Transfer, Methods for Chemical Analysis of Water andWastes, EPA-625/6-74-003, Washington, D.C., 1974. [NTIS No. PB 297686/AS]. pp. 266.

American Public Health Association, American Water Works Association, and Water Pollution Control Federation. Standard Methods for the Examination of Water and Wastewater, 14th edition. APHA, Washington, D.C., 1976. p. 89, [Method 208]

METHOD NUMBER: A-22

ANALYTICAL METHOD: Total Dissolved Solids Measurement

ANALYTES: Dissolved solids.

DESCRIPTION: Dissolved solids in aqueous samples are determined gravimetrically.

APPLICATIONS: Aqueous samples.

GENERAL METHOD PARAMETERS:

Preparative Requirements: Samples are kept cool (4°C) to minimize microbiological decomposition of solids. Grap (S-11) or composite (S-10) samples may be analyzed using this method. Mix sample well to ensure a representative aliquot is removed.

Method: Solids are removed with a standard glass fiber filter, the filtrate is evaporated, and the amount of filtrate solid residue remaining after heating to 180°C is determined gravimetrically. Total volatile dissolved solids are determined after heating to 550°C.

LIMITATIONS: Excessive residue mass may entrap water which is difficult to remove by drying. Samples with high bicarbonate levels must be carefully dried for extended periods at 180°C to convert to carbonate. Volatile components such as H_2S, NH_3, and CO_2 are lost in the determination.

SENSITIVITY: Sample should be weighted to nearest 0.1 mg.

QA/QC: Blanks and matrix replicates should be analyzed with each sample set. The precision of analysis should be reported.

METHOD NUMBER: A-22

EXTERNAL COST:

Per single analysis	$5-$15

INTERNAL COST:

Manhours/analysis	0.1 - 0.2
Capital Equipment:	
Oven, balance	$1,000-$3,000

REFERENCES: USEPA. Proposed Rules. Federal Register, 44(233), December 3, 1979. [Amendment to 40 CFR 136]

American Society for Testing and Materials, Annual Book of ASTM Standards, Part 31. Philadelphia, PA, 1981. [Method D-1888 - Tests for Particulate and Dissolved Matter in Water]

USEPA, Office of Technology Transfer, Methods for Chemical Analysis of Water and Wastes, EPA-625/6-74-003, Washington, D.C., 1974. [NTIS No. PB 297686/AS]. pp. 266.

American Public Health Association, American Water Works Association, and Water Pollution Control Federation. Standard Methods for the Examination of Water and Wastewater, 14th edition. APHA, Washington, D.C., 1976. p. 89, [Method 208]

METHOD NUMBER: A-23

ANALYTICAL METHOD: Total Suspended Solids Measurement

ANALYTES: Suspended Solids

DESCRIPTION: Total suspended solids are determined gravimetrically.

APPLICATIONS: Aqueous samples

GENERAL METHOD PARAMETERS:

Preparative Requirements: Samples are kept cool (4°C) to minimize microbiological decomposition of solids. Grab (S-11) or composite (S-10) samples may be analyzed using this method. Samples should be mixed well to ensure a representative aliquot is removed.

Method: Suspended solids are removed with a standard glass fiber filter, and the filter residue after heating to 105°C is determined gravimetrically. Volatile suspended solids are determined after heating to 550°C.

LIMITATIONS: See A-22

SENSITIVITY: Sample residues should be weighed to nearest 0.1 mg

QA/QC: Blanks and matrix replicates should be analyzed with each sample set. The precision of analysis should be reported.

EXTERNAL COST:

Per single analysis	\$5-\$15

METHOD NUMBER: A-23

INTERNAL COST:

Manhours/analysis	0.1-0.2
Capital Equipment:	
Oven, balance	$1,000-$3,000

REFERENCES: USEPA. Proposed Rules. Federal Register, 44(233), December 3, 1979. [Amendment to 40 CFR 136]

American Society for Testing and Materials, Annual Book of ASTM Standards, Part 31. Philadelphia, PA, 1981. [Method D-1888 - Tests for Particulate and Dissolved Matter in Water]

USEPA, Office of Technology Transfer, Methods for Chemical Analysis of Water and Wastes, EPA-625/6-74-003, Washington, D.C., 1974. [NTIS No. PB 297686/AS]. pp. 266.

American Public Health Association, American Water Works Association, and Water Pollution Control Federation. Standard Methods for the Examination of Water and Wastewater, 14th edition. APHA, Washington, D.C., 1976. p. 89, [Method 208]

METHOD NUMBER: A-24

ANALYTICAL METHOD: Determination of Chemical Oxygen Demand (COD)

ANALYTES: Chemical oxygen demand (COD)

DESCRIPTION: Chemical oxygen demand is determined by dichromate oxidation followed by colorimetric or titrimetric determination of the excess dichromate.

APPLICATIONS: Aqueous sample.

GENERAL METHOD PARAMETERS:

Preparative Requirements: Samples are preserved with H_2SO_4 at a pH <2 to prevent biological utilization of organic carbon. Grab (S-11) or composite (S-10) samples may be analyzed using this method.

Methods: An aliquot is placed in a reflux flask with $HgSO_4$. Concentrated sulfuric acid and 0.25N $K_2Cr_2O_7$ and then sulfuric acid-silver sulfate solution is added. (If volatiles are present in the sample, use an allihn condenser and add the sulfuric acid-silver sulfate solution through the condenser while cooling the flask, in order to minimize loss by volatilization). The mixture is refluxed, cooled and then rinsed with distilled water. The mixture is transferred to an erlenmeyer flask and again washed and diluted with distilled water. Ferron indicator is added and the excess dichromate titrated with 0.25N ferrous ammonium sulfate solution to the endpoint. A color change from blue-green to a reddish hue indicates the endpoint.

LIMITATIONS: Chloride interference must be removed with mercuric sulfate. For samples with high chloride levels, additional attention to chloride removal is required. Traces of organic material from glassware may cause gross positive error.

SENSITIVITY: Depends upon specific analysis. For the 5-50 mg/L range, sensitivity is 2 mg/L. With chloride levels above 1,000 mg/L, the minimum accepted value of sensitivity is 250 mg/L for COD.

QA/QC: A blank is simultaneous run to check on background contamination. A matrix replicate should be analyzed with each sample. The precision of analysis should be reported.

EXTERNAL COST:

Per single analysis	\$15-\$25

INTERNAL COST:

Manhours/analysis	0.2-0.4

Capital Equipment:

Oven, hot plate, condenser	\$100-\$1,000
Spectrophotometer	\$200-\$2,500

REFERENCES: US EPA. Proposed Rules. Federal Register, 44(233), December 3, 1979. (Amendment to 40 CFR 136)

American Society for Testing and Materials, Annual Book of ASTM Standards, Part 31. Philadelphia, PA, 1981. (Method D-1252 - Tests for Chemical Oxygen Demand (Dichromate Oxygen Demand) of Waste Water

US EPA, Office of Tehcnology Transfer, Methods for Chemical Analysis of Water and Wastes, EPA-625/6-74-003, Washington, D.C., 1974. (NTIS No. PB 297686/AS.) pp. 20-25.

METHOD NUMBER: A-24

American Public Health Association, American Water Works Association, and Water Pollution Control Federation. Standard Methods for the Examination of Water and Wastewater, 14th edition. APHA, Washington, D.C., 1976. pp. 550 (Method 508.)

METHOD NUMBER: A-25

ANALYTICAL METHOD: Determination of Biological Oxygen Demand (BOD)

ANALYTES: Dissolved oxygen

DESCRIPTION: The BOD test is an empirical procedure for measuring the dissolved oxygen microbially consumed by the assimilation and oxidation of organic material.

APPLICATIONS: Aqueous samples.

GENERAL METHOD PARAMETERS:

Preparative Requirements: Samples are kept cool (4°C) and analyzed within 24 hours. Otherwise, the time of test initiation, after collection, should be referenced. Grab (S-11) or composite (S-10) samples may be analyzed using this method.

Method: The sample is incubated for 5 days at 20°C in the dark. The dissolved oxygen reduction during the period is a measure of biological oxygen demand.

LIMITATIONS: Toxic components in the wastewater may inhibit biological oxidation.

SENSITIVITY: 5 mg/L

QA/QC: Blanks, matrix dilutions and matrix replicates are analyzed with each sample set.

EXTERNAL COST:

Per single analysis	$15-$35

INTERNAL COST:

Manhours/analysis	0.2-0.4

Capital Equipment:

Dissolved oxygen meter and probe	$300-$1,000
Incubation oven	$500-$2,000

REFERENCES: US EPA. Proposed Rules. Federal Register, 44 (233), December 3, 1979. (Amendment to 40 CFR 136)

US EPA, Office of Technology Transfer, Methods for Chemical Analysis of Water and Wastes, EPA-625/6-74-003, Washington, D.C. 1974. (NTIS No. PB 297686/AS.) pp. 11.

American Public Health Association, American Water Works Association, and Water Pollution Control Federation. Standard Methods for the Examination of Water and Wastewater, 14th edition. APHA, Washington, D.C., 1976. pp. 543. (Method 507)

METHOD NUMBER: A-26

ANALYTICAL METHOD: Distillation/Colorimetry (4-aminoantipyrine)

ANALYTES: Total Phenolics.

DESCRIPTION: Steam-distillable phenolic materials are reacted with 4-amino antipyrine (4-AAP) under select conditions to form a reddish-brown antipyrine dye. The amount of color produced is a function of the amount of phenolic material. The dye is concentrated by extraction into chloroform.

APPLICATIONS: Aqueous samples.

GENERAL METHOD PARAMETERS:

Preparative Requirements: Preserve with H_3PO_4 to pH <4; add 1 g $CuSO_4$ per liter to limit biological degradation. Cool to 4°C and analyze within 24 hours. Grab (S-11) or composite (S-10) samples may be analyzed for this method.

Method: An aliquot of the sample is distilled using a graham condenser. NH_4Cl is added to the distillate. The pH is adjusted with ammonium hydroxide and the solution is transferred to a 1L separatory funnel. Amino antipyrine solution is added, and mixed, followed by the addition of potassium ferricyanide solution. The contents are mixed well, and color allowed to develop. The solution is immediately extracted with $CHCl_3$. The absorbance of the $CHCl_3$ extract is read at 460 nm using a spectrophotometer.

LIMITATIONS: For most samples a preliminary distillation is required to remove interferences. Therefore, only steam-distillable phenols are addressed in the analysis. Color response of phenolic materials with 4-AAP is not the same for all compounds. For this reason, phenol has been selected as the standard and any color produced by reaction of other phenolic compounds is reported as phenol. The reported value will represent a minimum concentration of phenolic compounds present in the sample. Sulfur compounds and oil and grease are interferences.

SENSITIVITY: 50-200 µg/L; 1-20 µg/L with solvent extraction.

QA/QC: Calibration solutions are prepared and analyzed in order to generate a calibration curve, blanks, calibration standards, blank spikes, matrix spikes and matrix replicates should be analyzed with each sample set. The precision and recovery of the analysis should be reported.

EXTERNAL COST:

Per single analsis	\$20-\$50

INTERNAL COST:

Manhours/analysis	0.2-1

Capital Equipment:

Distillation unit and spectrophotometer	\$600-\$2,500

REFERENCES: US EPA. Proposed Rules. Federal Register, 44(233), December 3, 1979. (Amendment to 40 CFR 136)

American Society for Testing and Materials, Annual Book of ASTM Standards, Part 31. Philadephia, PA, 1981. (Method D-1783 - Tests for Phenolic Compounds in Water)

US EPA, Office of Technology Transfer, Methods for Chemical Analysis of Water and Wastes, EPA-625/6-74-003, Washington, D.C., 1974. (NTIS No. PB 297686/AS) pp. 241.

American Public Health Assocaition, American Water Works Association, and Water Pollution Control Federation. Standard Methods for the Examination of Water and Wastewater, 14th edition. APHA, Washington, D.C., 1976. p. 574.(Method 510)

METHOD NUMBER: A-27

ANALYTICAL METHOD: Distillation/Titration

ANALYTES: Ammonia

DESCRIPTION: The sample is buffered with borate buffer after pH adjustment with sodium hydroxide to pH of 9.5, and the ammonia is distilled into a boric acid solution. The ammonia in the distillate is determined titrimetrically with standard sulfuric acid in the presence of a mixed indicator.

APPLICATIONS: Aqueous samples and impinger solutions from gas sample collection.

GENERAL METHOD PARAMETERS:

Preparative Requirements: Preserve with H_2SO_4 to a pH <2, cool to 4°C. Samples should be analyzed as soon after collection as possible. Grab (S-11) or composite (S-10) aqueous samples, or impinger sorbent gaseous samples (S-07) may be analyzed using this method.

Method: The sample is first treated with a dechlorinating agent to remove residual chlorine. The pH of the sample is adjusted to 9.5 with sodium hydroxide. The sample is transferred to a Kjeldhal flask containing borate buffer, distilled into an Erlenmeyer flask containing boric acid solution. The distillate is diluted with distilled water.

The ammonia content is determined titrimetrically by adding a mixed indicator (methyl red/methylene blue solution freshly prepared) to the distillate, titrating the ammonia with 0.02N H_2SO_4, and matching the endpoint against a blank containing the same volume of distilled water and H_3BO_3solution (Pale lavender color).

To determine the concentration of ammonia present at $\leq$ 1 mg/L a colorimetric determination is used. An aliquot of the sample is nesslerized and the absorbance read at 425 nm. The ammonia content is determined from a prepared standard curve of absorbance vs mg NH_3.

LIMITATIONS: Cyanate if present may hydrolyze under test conditions. Residual chlorine or oxidizing agents must be removed by pretreatment before distillation as described in the method.

SENSITIVITY: Can range from 1.0 to 20 mg/L depending on the sample volume analyzed.

QA/QC: Calibration solutions are prepared and analyzed in order to generate a calibration curve. Blanks, calibration standards, blank spikes, matrix spikes and matrix replicates should be analyzed with each sample set.

EXTERNAL COST:

Per single analysis	\$15-\$25

INTERNAL COST:

Manhours/analysis	0.5-1
Capital Equipment:	
Distillation Unit	\$300-\$1,500

REFERENCES: US EPA. Proposed Rules. Federal Register, 44 (233), December 3, 1979. (Amendment to 40 CFR 136)

American Society for Testing and Materials, Annual Book of ASTM Standards, Part 31. Philadelphia, PA, 1981. (Method D-1426 - Tests for Ammonia Nitrogen in Water)

US EPA, Office of Technology Transfer, Methods for Chemical Analysis of Water and Wastes, EPA-625/6-74-003, Washington, D.C., 1974. (NTIS No. PB 297686/AS) pp. 159.

American Public Health Association, Amerian Water Works Association, and Water Pollution Control Federation. Standard Methods for the Examination of Water and Wastewater, 14th edition. APHA, Washington, D.C., 1976. pp. 407. (Method 418)

METHOD NUMBER: A-28

ANALYTICAL METHOD: Distillation/Colorimetry

ANALYTES: Cyanide, Total

DESCRIPTION: Cyanide as HCN is released from cyanide complexes by reflux-distillation and absorbed in a scrubber containing NaOH. The cyanide ion in the absorbing solution is determined by titration or colorimetry.

APPLICATIONS: Aqueous samples and impinger solutions from gas sample collection.

GENERAL METHOD PARAMETERS:

Preparative Requirements: Preserve with NaOH to pH >12; cool, 4°C. Samples should be analyzed within 24 hours of collection, or as soon as possible, and the time from collection to analysis referenced. Grab (S-11) or composite (S-10) aqueous samples or impinger sorbed gaseous samples (S-07) may be analyzed using this method.

The sample is prepared for analysis by first removing several interferences. Oxidizing agents (indicated by KI-starch test paper) are removed with ascorbic acid. Sulfides (indicated by lead acetate test paper) are removed with cadmium carbonate. Fatty acids are removed by a single extraction with hexane at pH 6-7. Following the extraction the pH is raised above pH 12.

Method: An aliquot of the sample is distilled in the presence of sulfuric acid and Cu_2Cl_2or $MgCl_2$ the gases trapped in sodium hydroxide.

The total cyanide concentration is determined by adding Chlormine T to the solution and mixing throughly. After 1-2 minutes a pyridine-barbituric acid (or pyridine-pyrazolone) solution is added and the absorbance read at 578 nm (630 nm when using pyridine-pyrazolone) after the start of color development, 8-15 minutes, (40 minutes for pyridine-pyrazolone). Alternatively, the solution may be titrated with silver nitrate in the presence of benzylrhodamine indicator to the first color change from yellow to brownish pink.

LIMITATIONS: The distillation step removes most interferences. Sulfides must be removed prior to preservation by precipitation with a lead or cadmium salt and filtration. Oxidizing agents such as chlorine and other interferences must be removed to prevent cyanide decomposition during reflux-distillation as described in the method.

SENSITIVITY: Colorimetry - 0.02 to 0.2 mg/L; titration - >1 mg/L, depending on sample volume and the complexity of the sample matrix.

QA/QC: Calibration solutions are prepared and analyzed in order to generate a calibration curve. Blanks, calibration standards, blank spikes, matrix spikes and matrix replicates should be analyzed with each sample set. The precision and recovery of analysis should be reported.

EXTERNAL COST:

Per single analysis	\$20-\$40

INTERNAL COST:

Manhours/analysis	0.2-0.4

Capital Equipment:

Distillation unit and spectrophotometer $600-$2,500

REFERENCES: US EPA. Proposed Rules. Federal Register, 44 (233), December 3, 1979. [Amendment to 40 CFR 136]

American Society for Testing and Materials, Annual Book of ASTM Standards, Part 31. Philadelphia, PA, 1975. [Method D-2036 - Tests for Cyanides in Water]

US EPA, Office of Technology Transfer, Methods for Chemical Analysis of Water and Wastes, EPA-625/6-74-003, Washington, D.C., 1974. [NTIS No. PB 297686/AS]/ pp. 40.

American Public Health Association, American Water Works Association, and Water Pollution Control Federation. Standard Methods for the Examination of Water and Wastewater, 14th edition. APHA, Washington, D.C., 1976. pp. 361 [Method 413]

ALTERNATES: Ingersoll, D., W.R. Harris, and D.C. Bomberger, "Ligand Displacement Method for the Determination of Total Cyanide," Anal. Chem. 53, 2254-2258, 1981.

Luthy, A. Manual of Methods: Preservation and Analysis of Coal Gasification Wastewaters. Environmental Studies Institute, Carnegie-Mellon University, Pittsburgh, PA, July, 1977.

METHOD NUMBER: A-29

ANALYTICAL METHOD: Precipitation/Titration

ANALYTES: Sulfide

DESCRIPTION: Excess iodine is added to a sample previously treated with zinc acetate to produce zinc sulfide. The iodine oxidizes the sulfide to sulfur under acidic conditions. Excess iodine is back-titrated with sodium thiosulfate. The iodine consumption is proportional to sulfide concentration.

APPLICATIONS: Aqueous samples.

GENERAL METHOD PARAMETERS:

Preparative Requirements: Samples may need to be filtered to remove suspended solids prior to preservation of the filtrate by zinc acetate addition. Samples should be analyzed for sulfide within 24 hours or as soon as possible and the time from collection to analysis referenced. Grab (S-11) or composite (S-10) sample may be analyzed, however, compositing may cause loss of highly volatile sulfides.

Method: A volume of standard iodine solution (estimated to be in excess of the amount of sulfide present) is added to the sample. If the iodine color disappears, more is added until the color remains. The total volume added is recorded. To this sample is also added 2 mL of 6N HCl.

The solution is titrated with 0.0250N sodium thiosulfate (reducing solution) using a starch indicator until the blue color disappears. The total volume titrated is recorded and sulfide concentrations calculated.

LIMITATIONS: Suspended solids may mask the end point if not removed prior to the test. Reduced sulfur components may decompose and yield erratic results. Therefore, the zinc sulfide precipitate may be separated by filtration and saved for analysis. Samples must be taken with minimum aeration to minimize volatile or oxidative losses.

SENSITIVITY: 0.1 to 5 mg/L

QA/QC: Calibration standards are prepared and analyzed in order to generate a calibration curve. Reagents should be standardized and blanks, calibration standards, blank spikes, matrix spikes, and matrix replicates should be analyzed with each sample set. The precision and recovery of analysis should be reported.

EXTERNAL COST:

Per single analysis	\$10-\$25

INTERNAL COST:

Manhours/analysis	0.1-0.2
Capital Equipment:	
Miscellaneous laboratory equipment	\$200

REFERENCES: US EPA. Proposed Rules. Federal Register, 44 (233), December 3, 1979. (Amendment to 40 CFR 136)

US EPA, Office of Technology Transfer, Methods for Chemical Analysis of Water and Wastes, EPA-625/6-74-003, Washington, D.C. 1974. (NTIS No. PB 297686/AS) pp. 284.

American Public Health Association, American Water Works Association, and Water Pollution Control Federation. Standard Methods for the Examination of Water and Wastewater, 14th edition. APHA, Washington, D.C., 1976. pp. 499 [Method 428]

METHOD NUMBER: A-30

ANALYTICAL METHOD: Colorimetry

ANALYTES: Thiocyanate ion

DESCRIPTION: Thiocyanate ion forms an intense red color in the presence of ferric ion at acidic pH.

APPLICATIONS: Aqueous samples.

GENERAL METHOD PARAMETERS:

Preparative Requirements: Remove sulfides if present by cadmium or lead salt addition and filtration of the sulfide precipitate. Cyanide interference must be removed by chlorination. Reducing agents must be overcome with H_2O_2. Hexavalent chromium is reduced by $FeSO_4$ addition under acid conditions, raising the pH to 9 precipitates Fe (+3) and Cr(+3). Grabs (S-11) or composite (S-10) samples may be analyzed using this method.

Method: A sample aliquot is filtered. The pH is adjusted to pH 5 to 7 by the addition of nitric acid dropwise. Ferric nitrate solution is added and the pH is adjusted to between pH 1 and 2. The sample is diluted with distilled water and shaken well. The absorbance is measured at 480 nm. Distilled water is used as a reference blank.

LIMITATIONS: The method must be verified for samples which are either highly colored or contain organic compounds. It is important that sulfide, cyanide, hexavalent chromium and reducing agents are removed from the samples prior to analysis as noted in the preparative requirements.

SENSITIVITY: 1-4 mg/L

QA/QC: Calibration standards are prepared and analyzed in order to generate a calibration curve. Blanks, calibration standards, blank spikes, matrix spikes and matrix replicates should be analyzed with each sample set. The precision and recovery of analysis should be reported.

EXTERNAL COST:

Per single analysis	\$10-\$30

INTERNAL COST:

Manhours/analysis	0.1-0.3
Capital Equipment:	
Spectrophotometer	\$500-\$2,000

PRIMARY REFERENCE: American Public Health Association, American Water Works Association, and Water Pollution Control Federation. Standard Methods for the Examination of Water and Wastewater, 14th edition. APAA, Washinton, D.C., 1976. pp. 383. [Method 413 Part K]

ALTERNATE REFERENCE: Luthy, Richard A., "Manual of Methods: Preservation and Analysis of Coal Gasification Wastewaters," Environmental Studies Institute, Carnegie-Mellon University, Pittsburgh, PA, July 1977

METHOD NUMBER: A-31

ANALYTICAL METHOD: Specific Ion Electrode

ANALYTES: Fluroide ion

DESCRIPTION: Specific ion electrode determination of fluoride is accomplished with a pH meter utilizing an expanded millivolt scale, or a selective ion meter with direct concentration scale.

APPLICATIONS: Aqueous streams.

GENERAL METHOD PARAMETERS:

Preparative Requirements: This analytical technique is applicable for grab (S-11) or composite (S-10) samples, or impinger solutions (S-07), if EPA Method 13 is not required.

Method: A aliquot of the sample and a buffer are added to a beaker. The beaker is placed on a magnetic stirrer at a medium speed. The electrodes are immersed in the solution and allowed to equilbrate for 3 to 5 minutes. The fluoride level is read directly as mg/L fluoride on the fluoride scale of the selective ion meter. When a pH meter is used, the potential measurement is recorded for each sample. This is converted to a fluoride ion concentration using a standard curve of pH potential vs fluoride ion concentration.

LIMITATIONS: Si(+4), Fe(+3), and Al(+3) which can interfere by complexing the fluoride ion are chelated. The effects of variable pH and ionic strength on the analysis can be overcome by strong buffering of the solution.

SENSITIVITY: 0.01 to 0.1 mg/L

QA/QC: Calibration standards are prepared and analyzed in order to generate a calibration curve. Blanks, calibration standards, blank spikes, matrix spikes and matrix replicates should be analyzed with each sample set. The precision of an analysis should be reported.

EXTERNAL COST:

Per single analysis	\$15-\$30

INTERNAL COST:

Manhour/analysis	0.1-0.3
Capital Equipment:	
pH meter, electrodes	\$500-\$1,500

PRIMARY REFERENCES: US EPA Proposed Rules. Federal Register, 44(233), December 3, 1979. [Amendment to 40 CFR 136]

American Society for Testing and Materials. Annual Book of ASTM Standards, Part 31. Philadelphia, PA. 1981. [Method D-1179 - Tests for Fluoride Ion in Water]

US EPA Office of Technology Transfer, Methods for Chemical Analysis of Water and Wastes, EPA-625/6-74-003, Washington, D.C., 1974. [NTIS No. PB 297686/AS]. pp. 59.

American Public Health Association, American Water Works Association, and Water Pollution Control Federation. Standard Methods for the Examination of Water and Wastewater, 14th edition. APAA, Washington, D.C., 1976. pp. 387. [Method 414]

METHOD NUMBER: A-32

ANALYTICAL METHOD: Cadmium Reduction/Spectrophotometry

ANALYTES: Nitrate, Nitrite

DESCRIPTION: A filtered sample is passed through a granulated copper-cadmium column to reduce nitrate to nitrite. Nitrite is determined spectrophotometrically after formation of a highly colored azo dye.

APPLICATIONS: Aqueous samples.

GENERAL METHOD PARAMETERS:

Preparative Requirements: The sample is kept cool (4°C) and should be analyzed within 24 hours or as soon as possible. Samples requiring longer storage prior to analysis should be preserved with H_2SO_4 to a pH <2, in addition to being kept cool. Tubridity is removed by filtration and oil and grease by solvent extraction. Grab (S-11) of composite (S-10) samples may be analyzed using this method.

Method: The pH of the sample is adjusted to between 5 and 9 with hydrochloric acid or ammonium hydroxide. The sample is passed thorugh a reduction column (cadmium-copper granules). The nitrite-nitrate nitrogen is determined by diazotizing the total nitrite ion with sulfanilimide and cooling with N-(1-naphthyl)-ethylene diamine dihydrochloride and the adsorbance read. Nitrate only may be determed by omitting the cadmium reduction step. Nitrate is then calculated as the difference between nitrate-nitrite and nitrite.

LIMITATIONS: The reduction column can be affected by suspended matter, oil and grease. These interferences should be removed prior to the column reduction step. Sulfide may also interfere with the reduction column operation and/or efficiency. Excessive amounts of chlorine will deactivate the reducing column.

METHOD NUMBER: A-32

SENSITIVITY: 0.01 to 0.1 mg/L

QA/QC: Calibration standards are prepared and analyzed in order to generate a calibration curve. Standards are analyzed in decreasing order of concentration. Blanks, calibration standards, blank spikes, matrix spikes, and matrix replicates (diluted samples) should be analyzed with each sample set. The precision and recovery of analysis should be reported.

EXTERNAL COST:

Per single analysis	$15-$30

INTERNAL COST:

Manhours/analysis	0.1-0.4

Capital Equipment:

Column, spectrophotometer	$600-$2,500

PRIMARY REFERENCES: US EPA. Proposed Rules. Federal Register, 44 (233), December 3, 1979. [Amendment to 40 CFR 136]

American Society for Testing and Materials. Annual Book of ASTM Standards, Part 31, Philadelphia, PA, 1981. [Method D-3868-79-Nitrite-Nitrate in Water]

US EPA, Office of Technology Transfer, Methods for Chemical Analysis of Water and Wastes, EPA-625/6-74-003, Washington, D.C., 1974. [NTIS No. PB 297686/AS]. pp. 201.

METHOD NUMBER: A-32

American Public Health Association, American Water Works Association, and Water Pollution Control Federation. Standard Methods for the Examination of Water and Wastewater, 14th edition. APAA, Washington, D.C., 1976. pp. 418. [Method 419]

METHOD NUMBER: A-33

ANALYTICAL METHOD: Silver Nitrate Titration with Potentiometric End-point Determination

ANALYTES: Chloride

DESCRIPTION: Chloride is determined by potentiometric titration.

APPLICATIONS: Aqueous samples.

GENERAL METHOD PARAMETERS:

Preparative Requirements: Preservation not required. Sulfite, sulfide, cyanide (Fe(+3))and organic interferences are removed by acidification with H_2SO_4 and boiling, and finally, treatment with alkaline H_2O_2 and further boiling.

Grab (S-11), composite (S-10) or impinger (S-07) samples may be analyzed using this method.

Method: The pH of the sample is adjusted to 8.3. Chloride is determined by potentiometric titration with silver nitrate solution using a glass and Ag/AgCl electrode system. A millivolt meter is used to detect changes in potential. The endpoint of the titration is that reading at which the greatest potential change per titrant volume is observed.

LIMITATIONS: Organic compounds, SO_3, FE(+3), CN(-1) and S(-2) interfere. Pretreatment requires boiling under acidic (H_2SO_4) conditions, then with H_2O_2, and finally alkaline (NaOH conditions.)

SENSITIVITY: 2-10 mg/L

QA/QC: The potentiometer (pH - meter) and $AgNO_3$ titrant are standardized using a standard NaCl solution. A differential titration curve is plotted to determine the exact endpoint. Blanks, blank spikes, matrix spikes and matrix replicates should be analyzed with each sample set. The precision and recovery of analysis should be reported.

EXTERNAL COST:

Per single analysis	\$10-\$35

INTERNAL COST:

Manhours/analysis	0.2-0.4

Capital Equipment:

Millivoltmeter, electrodes, hot plate	\$600-\$2,000

PRIMARY REFERENCES: US EPA. Proposed Rules. Federal Register, 44 (233), December 3, 1979. [Amendment to 40 CFR 136]

American Society for Testing and Materials. Annual Book of ASTM Standards, Part 31. Philadelphia, PA, 1981. [Method D-512 - Chloride]

US EPA, Office of Technology Transfer, Methods for Chemical Analysis of Water and Wastes, EPA-625/6-74-003, Washington, D.C., 1974. [NTIS No. PB 297686/AS]. pp. 29.

American Public Health Association, American Water Works Association, and Water Pollution Control Federation. Standard Methods for the Examination of Water and Wastewater, 14th edition. APAA, Washington, D.C., 1976. pp. 302. [Method 408]

METHOD NUMBER: A-33

ALTERNATE REFERENCE: Fritz, J.S., D.T. Gjerde, and C. Pohlandt. Ion Chromatography. Huthig Verlag. Heidelberg, New York. 1982.

METHOD NUMBER: A-34

ANALYTICAL METHOD: Iodometric Titration

ANALYTES: Sulfite

DESCRIPTION: An acidified sample containing a starch indicator is titrated with a standard KI/KIO_3 titrant to a faint permanent blue end-point which appears when the reducing power of the sample is exhausted.

APPLICATIONS: Aqueous samples.

GENERATED METHOD PARAMETERS:

Preparative Requirements: The sample is kept cool (4°C) and aeration or filtration is minimized. Sulfide if present must be removed by precipitation with zinc acetate. (P-11). Grab samples (S-11) are most appropriate for this analysis. Sample contact with air must be kept to a minimum. A portion of an EDTA Solution (a preservative) should be added to the sample prior to analysis.

Method: An aliquot of sample is placed in a titration vessel. Sulfuric acid crystals, and the starch indicator is added. The sample is titrated with a potassium iodide-iodate titrant until a permanent faint blue color develops. It is important to keep the pipet tip below the surface of the sample. The volume of titrant is recorded and sulfite concentration calculated.

LIMITATIONS: Fe(+2) and S(-2) and other oxidizable components are positive interferences and must be addressed (P-11). Nitrate if present will oxidize sulfite upon acidification. Heavy metals will catalyze sulfite oxidation.

SENSITIVITY: 2-10 mg/L.

QA/QC: Blanks, standard solutions, matrix spikes and matrix replicates should be analyzed with each sample set. The precision of analysis should be reported.

EXTERNAL COST:

Per single analysis	$10-$25

INTERNAL COST:

Manhours/analysis	0.2-0.4
Capital Equipment:	
Glassware	$100

REFERENCES: US EPA. Proposed Rules. Federal Register, 44(233), December 3, 1979. [Amendment to 40 CFR 136]

American Society for Testing and Materials. Annual Book of ASTM Standards, Part 31. Philadelphia, PA, 1981. [Method D-1339 - Tests for Sulfite Ion in Water]

US EPA, Office of Technology Transfer, Methods for Chemical Analysis of Water and Wastes, EPA-625/6-74-003, Washington, D.C., 1974. [NTIS No. PB 297686/AS]. pp. 285.

American Public Health Association, American Water Works Association, and Water Pollution Control Federation. Standard Methods for the Examination of Water and Wastewater, 14th edition. APAA, Washington, D.C., 1976. pp. 508. [Method 429]

METHOD NUMBER: A-35

ANALYTICAL METHOD: Turbidimetric Analysis

ANALYTES: Sulfate

DESCRIPTION: Sulfate ions are converted to a barium sulfate suspension under controlled conditions. The resulting turbidity is determined spectrophotometrically and compared to a sulfate standard calibration curve.

APPLICATIONS: Aqueous samples.

GENERAL METHOD PARAMETERS:

Preparative Requirements: The sample is kept cool (4°C)- Grab (S-11) or composite (S-10) samples may be analyzed by this method.

Method: A portion of conditioning solution (solution containing glycerol, Conc HCl, NaCl, isopropyl alcohol in distilled water), is added to the sample and the solution is stirred. $BaCl_2$ crystals are added.

The turbidity is measured at regular intervals at 420 nm for 4 minutes; at which time a maximum reading is recorded. The sample is run against a blank treated as stated above without the addition of $BaCl_2$. Concentration of the samples are determined by comparison to a calibration curve.

LIMITATIONS: Suspended matter and color will interfere; this is corrected by analysis of sample blanks (without barium).

SENSITIVITY: 1-5 mg/L

QA/QC: Calibration standards are prepared and analyzed in order to generate a calibration curve. Blanks, calibration standards, matrix spikes and matrix replicates should be analyzed with each sample set.

EXTERNAL COST:

Per single analysis	\$10-\$20

INTERNAL COST:

Manhours/analysis	0.1-0.2
Capital Equipment:	
Spectrophotometer	\$500-\$2,500

REFERENCES: US EPA. Proposed Rules. Federal Register, 44(233), December 3, 1979. [Amendment to 40 CFR 136].

American Society for Testing and Materials. Annual Book of ASTM Standards, Part 31. Philadelphia, PA, 1975. [Method D-516 - Tests for Sulfate Ion in Water and Wastewater].

US EPA, Office of Technology Transfer, Methods for Chemical Analysis of Water and Wastes, EPA-625/6-74-003, Washington, D.C., 1974. [NTIS No. PB 297686/AS]. pp. 277.

American Publich Health Association, American Water Works Association, and Water Pollution Control Federation. Standard Methods for the Examination of Water and Wastewater, 14th edition. APAA, Washington, D.C., 1976. pp. 493 [Method 427].

METHOD NUMBER: A-36

ANALYTICAL METHOD: Radioactivity

ANALYTES: Gross alpha, gross beta.

DESCRIPTION: An aliquot of the aqueous sample is evaporated and dried; the residue analyzed. Alpha and beta emissions are counted by gas proportional counter.

APPLICATIONS: Aqueous samples.

GENERAL METHOD PARAMETERS:

Preparative Requirements: Preserve filtered (to determine dissolved radioactivity) or unfiltered (to determine total radioactivity) samples with HNO_3 to pH <2. Grab (S-11) or composite samples may be analyzed using this method.

Method: A sample aliquot containing not more than 200 mg of residue for beta examination and not more than 100 mg residue for alpha examination is taken for each 20 cm^2 of counting per area. The sample is evaporated slowly just below boiling. The sample is placed in a 105°C oven to complete dryness, then allowed to cool in a clean dry desiccator. The sample is weighed and placed in an internal counter (or geiger counter) for alpha and beta activity counts.

If the residue has airborne particles, a few drops of a Lucite solution is added and allowed to set. This acts as a binder to prevent counter contamination by such particles.

For determination of the activity of dissolved solids. The sample is filtered through a Gooch crucible. The filtrate is treated in the same manner as above.

LIMITATIONS: Maximum of 200 mg residue/200 cm^2 counting pan for alpha analysis; 100 mg for beta.

SENSITIVITY: Dependent on counter.

QA/QC: Standards are used for instrument calibration. Blanks and matrix replicates should be analyzed with each sample set. The precision of analysis should be reported.

EXTERNAL COST:

Per single analysis	\$30-\$50

INTERNAL COST:

Manhours/analysis	0.1-0.2
Capital Equipment:	
Gas proportional counter	\$10,000-\$30,000

REFERENCES: American Public Health Association, American Water Works Association, and Water Pollution Control Federation. Standard Methods for the Examination of Water and Wastewater, 14th edition. APAA, Washington, D.C., 1976. pp. 633-679. [Method 703].

American Society for Testing and Materials. Annual Book of ASTM Standards, Part 31. Philadlphia, PA, 1975. [Method D-3084 - Alpha Spectrometry, D-1890 - Beta Particle Radioactivity, D-3085 - Activity, Low Level].

US EPA. Proposed Rules. Federal Register, 44 (233), December 3, 1979. [Amendment to 40 CFR 136].

METHOD NUMBER: A-37

ANALYTICAL METHOD: Extraction/Gravimetric Analysis

ANALYTES: Oil and grease

DESCRIPTION: Oil and grease is serially extracted from the water sample with Freon-113 in a separatory funnel. The solvent is evaporated from the extract and the residue is weighed. For samples containing extractable free sulfur, infrared detection of oil and grease should be used.

APPLICATIONS: Aqueous samples

GENERAL METHOD PARAMETERS:

Preparative Requirements: The sample is preserved with HCl to a pH <2 and kept cool (4°C) if analysis cannot be performed within a few hours of collection. Grab samples (S-11) are preferred for analysis using this method.

Method: The sample is extracted with Fluorocarbon-113 (Freon-113) and transferred. The extract is filtered through moistened filter paper into a clear, tared boiling flask (if any emulsion fails to break, pass anhydrous emulsion through Na_2SO_4). The extract is repeated twice and all extracts combined in the collection flask.

The boiling flask is connected to a distilling head, and the solvent evaporated slowly by immersing the flask in warm water (70°C). As the flask appears to be dry, the distilling head is removed and flask swept with air to remove all solvent vapor.

The flask is cooled in a desiccator and weighed for gravimetric determination.

LIMITATIONS: The method is applicable to relatively non-volatile hydrocarbons, vegetable oils, animal fats, and waxes. Light hydrocarbons that volatilize below 70°C are lost. Some crude and heavier fuel oils are only partially recovered due to components insoluble in Freon-113. Samples containing sulfide will form free sulfur upon preparative acidification. This sulfur is somewhat soluble in Freon-113 and may bias gravimetric results.

SENSITIVITY: 5-50 mg/L

QA/QC: Blanks, blank spikes, matrix spikes and matrix replicates should be analyzed with each sample set. The precision and recovery of analysis should be reported.

EXTERNAL COST:

Per single analysis	\$15-\$40

INTERNAL COST:

Manhours/analysis	0.2-1
Capital Equpment:	
Special glassware, vacuum pump, balance	\$2,000-\$5,000

REFERENCES: US EPA. Proposed Rules. Federal Register, 44(233), December 3, 1979. [Amendment to 40 CFR 136].

American Society for Testing and Materials. Annual Book of ASTM Standards, Part 31. Philadelphia, PA, 1981. [Method D-2778 - Solvent Extraction of Organic Matter from Water].

METHOD NUMBER: A-37

US EPA, Office of Technology Transfer, Methods for Chemical Analysis of Water and Wastes, EPA-625/6-74-003, Washington D.C., 1974. [NTIS No. PB 297686/AS]. pp. 226.

American Public Health Association, American Water Works Association, and Water Pollution Control Federation. Standard Methods for the Examination of Water and Wastewater, 14th edition. APHA, Washington, D.C., 1976. pp. 513. [Method 502].

METHOD NUMBER: A-38

ANALYTICAL METHOD: Ascorbic Acid Colorimetric Method for Dissolved, Hydrolyzable, or Total Phosphorus

ANALYTES: Phosphorus

DESCRIPTION: Phosphorus (phosphate) solutions react with ammonium molybdenate and potassium tartrate in an acid medium to form a complex which, when reduced with ascorbic acid, is intensely blue colored. The color is proportional to the phosphorus concentration. Other phosphorus forms can be converted to phosphate by acid digestion with sulfuric acid or by persulfate digestion.

APPLICATIONS: Aqueous samples.

GENERAL METHOD PARAMETERS:

Preparative Requirements: The method of preparation depends on the information required:

Analyte	Preservation	Preparation
P (PO_4 Dissolved)	Filter Cool to 4°C	None
P (Total, Hydrolyzable)	Cool to 4°C, H_2SO_4 to pH <2	H_2SO_4 hydrolysis
P (Total)	Cool to 4°C, H_2SO_4 to pH <2	Persulfate digestion
P (Total, Dissolved)	Filter Cool to 4°C, H_2SO_4 to pH <2	Persulfate digestion

Grab (S-11) or composite (S-10) samples may be analyzed using this method.

METHOD NUMBER: A-38

Method: Phosphorus, hydrolyzable phosphorus, and other forms are converted to the phosphate by sulfuric acid or persulfate digestion. Once prepared, the pH of the sample is adjusted to > ± 0.2 using a pH meter.

An aliquot of freshly prepared, combined reagent (ascorbic acid solution, ammonium molybdate solution, potassium antimohyltartrate solution and dilute sulfuric acid) is added to the sample. After setting, the color absorbance is measured at 650 or 880 nm with a spectrophotometer, using a reagent blank as a reference.

SENSITIVITY: 0.01 to 0.1 mg/L as phosphorus.

QA/QC: Calibration standards are prepared and analyzed in order to generate a calibration curve. Blanks, calibration standards, blank spikes, matrix spikes and matrix replicates should be analyzed with each sample set. The precision and recovery of analysis should be reported.

EXTERNAL COST:

Per single analysis	\$15-\$40

INTERNAL COST:

Manhours/analysis	0.2-0.4
Capital Equipment:	
Spectrophotometer	\$500-\$2,500

METHOD NUMBER: A-38

REFERENCES: USEPA. Proposed Rules. Federal Register, 44(233), December 3, 1979. [Amendment to 40 CFR 136]

American Society for Testing and Materials, Annual Book of ASTM Standards, Part 31. Philadelphia, Pennsylvania, 1981. [Method D-515 - Test for Phosphorus in Water]

USEPA, Office of Technology Transfer, Methods for Chemical Analysis of Water and Wastes, EPA 625/6-74-003, Washington, D.C., 1974, p. 249. [NTIS No. PB 297686/AS]

American Public Health Association, American Water Works Association and Water Pollution Control Federation. Standard Methods for the Examination of Water and Wastewater, 14th Edition. APHA, Washington, D.C., 1976, p. 466. [Method 425]

METHOD NUMBER: A-39

ANALYTICAL METHOD: Acid/Base Titration

ANALYTES: Acidity, alkalinity

DESCRIPTION: An unfiltered sample is titrated to an electromagnetic endpoint of pH 4.5 for alkalinity determination. Acidity is determined by titration to electrometric endpoints of pH 8.3 and 3.7. Standard indicators (phenolphthalein, methyl orange) may be used.

APPLICATIONS: Aqueous samples

GENERAL METHOD PARAMETERS:

Preparative Requirements: The sample is kept cool (4°C) and analyzed as soon as possible. Grab (S-11) or composite (S-10) samples are analyzed using this method.

Method:

Acidity. An aliquot of the sample is pipeted into a beaker. The pH is measured and lowered to pH 4 or less with a standard sulfuric acid solution. Hydrogen peroxide is added and the sample boiled for several minutes (to remove ferrous iron present).

The sample is cooled to room temperature and titrated electrometrically with a standard sodium hydroxide solution to a pH of 8.3. (Solution may be titrated to phenolphthalein endpoint as well.)

Alkalinity. An aliquot of the sample is pipeted into a beaker. The pH is measured and recorded. The sample is titrated electrometrically with standard acid (sulfuric or hydrochloric) solution to a pH of 4.5. The volume is recorded and alkalinity determined (low alkalinity requires slightly modified conditions).

LIMITATIONS: Samples with high concentrations of mineral acids may undergo a shift in the titration endpoint pH. Calculations are made on a stoichiometric basis; therefore, iron concentrations are not rigorously represented in the results.

SENSITIVITY: Highly dependent on concentration of the titrant; can vary from 1 to 100 mg/L $CaCO_3$.

QA/QC: The normality of the titrant should be verified regularly during analysis of samples. A check of titration endpoint, verification of pH as a function of titrant volume, may be necessary for unknown samples.

SAMPLING REQUIREMENTS: Analytical technique is applicable for grab (S-11) or composite (S-10) samples.

EXTERNAL COST:

Per single analysis	\$10-\$25

INTERNAL COST:

Manhours/analysis	0.1-0.3
Capital Expenditure:	
pH meter and electrodes	\$300-\$1,300

REFERENCES: USEPA. Proposed Rules. Federal Register, 44(233), December 3, 1979. [Amendment to 40 CFR 136]

American Society for Testing and Materials, Annual Book of ASTM Standards, Part 31. Philadelphia, Pennsylvania, 1981. [Method D-1067 - Tests for Acidity or Alkalinity of Water]

USEPA, Office of Technology Transfer, Methods for Chemical Analysis of Water and Wastes, EPA 625/6-74-003, Washington, D.C., 1974, p. 1. [NTIS No. PB 297686/AS]

American Public Health Association, American Water Works Association, and Water Pollution Control Federation. Standard Methods for the Examination of Water and Wastewater, 14th Edition. APHA, Washington, D.C., 1976, p. 273. [Method 402, Method 403]

METHOD NUMBER: A-40

ANALYTICAL METHOD: Elemental Analysis by Inductively Coupled Optical Emission Spectroscopy (ICP) or Atomic Absorption Spectroscopy (AA)

ANALYTES: Ag, Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Si, Te, Ti, Tl, V, Zn.

PREPARATIVE REQUIREMENTS: Preservation of a filtered sample (to determine dissolved metals) or an unfiltered sample (to determine total metals) with HNO_3 to pH <2.

LIMITATIONS: No single sample preparation technique is applicable for complete conversion of all element from solid to liquid phase. In many cases the water sample matrix interfer with the analysis. Viscosity differences between samples and standards can result in different sample aspiration rates and therefore bias results.

SENSITIVITY: Dependent on both element and method:

Sensitivity (mg/L)	Elements
0.001-0.01	Ag,Al,Ba,Be,Cd,Co,Cr,Cu,Mn,Mo,Ni,V,Zn,Al,
0.01-0.1	As,B,Ca,Fe,Hg,K,Mg,Na,Pb,Sb,Se,Si,Ti,
0.1-1.0	Te,Tl

QA/QC: Good laboratory practice including blanks and daily standard calibration curves.

SAMPLING REQUIREMENTS: Analytical technique is applicable for grab (S-11) or composite (S-10) samples.

EXTERNAL COST:

Per single analysis:

AA/element	$8-$24
ICP/sample	$50-$200

INTERNAL COST:

Manhours/analysis

AA/element	0.1-0.3
ICP/sample	0.1-0.2

Capital Equipment:

AA and lamps	$10,000-$50,000 (depending on optical resolution)
ICP	$50,000-$250,000 (depending on multielement capabilities, resolution, data systems)

PRIMARY REFERENCES: USEPA. Proposed Rules. Federal Register, 44(233), December 3, 1979. [Amendment to 40 CFR 136].

American Society for Testing and Materials, Annual Book of ASTM Standards, Part 31. Philadelphia, PA, 1975. [Numerous methods, by element of interest].

USEPA, Office of Technology Transfer, Methods for Chemical Analysis of Water and Wastes, EPA-625/6-74-003, Washington, D. C., 1974. [NTIS No. PB 297686/AS]. pp. 78-156.

American Public Health Association, American Water Works Association, and Water Pollution Control Federation. Standard Methods for the Examination of Water and Wastewater, 14th edition. APHA, Washington, D. C., 1976. p. 143. [Part 300 - Determination of Metals].

METHOD NUMBER: A-41

ANALYTICAL METHOD: Spectrophotometric Determination of Nitrogen Oxides in Vapor Phase Samples

ANALYTES: Nitrogen dioxide

DESCRIPTION: Sorbent solutions are analyzed spectrophotometrically and the intensity related to sample concentration

APPLICATIONS: Spectrophotometry is applicable for the analysis of Saltzman solutions, and the sulfuric acid/peroxide catch from EPA Method 7 after the evaporation and phenoldisulfonic acid reaction.

GENERAL METHOD PARAMETERS:

Preparative Requirements: Saltzman solutions stable for a week prior to analysis if kept cool (<25°C), dark and in an SO_2-free atmosphere. Method 7 solutions must be held 16 hours prior to analysis for reaction completion. Vapor phase samples (S-02) are analyzed using this method.

Method: A sample aliquot is taken to dryness on a steam bath. After cooling, phenoldisulfonic acid solution is added to the residue (ground to a fine powder). Distilled water and concentrated sulfuric acid are added to the powdered residue, followed by heating.

The solution is transferred to a volumetric flask and brought to volume with distilled water. The absorbance is measured between 400 and 415 nm (maximum absorbance determined using standard solutions). The absorbance of the sample is compared with those of calibration standards run (dilutions may be required to bring the sample into the range of the calibration curve).

LIMITATIONS: Nitrous oxide (NO) is not measured using EPA Method 7 or the Saltzman technique. Chloride interferes with Method 7 analytical preparation. Ozone at 5:1 and SO_2 at 30:1 interfere with Saltzman technique, addition of 1% acetone to Saltzman reagent minimizes the SO_2 interference. Saltzman stoichiometric factor is disputed.

SENSITIVITY: Saltzman method ∿0.1-1 μg NO_2/mL, gas volume can be increased to achieve low stream concentration. EPA Method 7 minimum detection level ∿10 vppm.

QA/QC: Calibration standards are prepared and analyzed. Blanks, matrix replicates, and matrix dilutions should be analyzed with each sample set. The precision of analysis should be reported.

EXTERNAL COST:

Per single analysis	\$20-\$100

INTERNAL COST:

Manhours/analysis	0.2-4 (depending on technique)
Capital Equipment:	
UV Spectrophotometer	\$200-\$2,500 (depending on range and optical quality)

METHOD NUMBER: A-41

PRIMARY REFERENCES: Title 40, CFR Part 60, Appendix A, December 5, 1980. [Method 7 - Determination of Nitrogen Oxide Emissions from Stationary Sources]

Texas Air Control Board, Laboratory Methods for Determination of Air Pollutants, Laboratory Division, Austin, TX, 1978.

Purdue, L.J., J.E. Dudley, J.B. Clements, and R.J. Thompson. Reinvestigation of the Jacobs-Hochheiser Products for Determining Nitrogen Dioxide in Ambient Air, Environ. Sci. & Tech., 6(2):152-154, February 1972.

ALTERNATE METHODS: Jacobs, M.B., and S. Hochheiser, Continuous Sampling and Ultra-Microdetermination of Nitrogen Dioxide in Air. Anal. Chem., 30, 1958, p. 426.

Christie, A.A., R.G. Lidzey, and D.W.F. Radford, Field Methods of the Determination of Nitrogen Dioxide in Air, The Analyst, 95, May 1970, p. 519.

METHOD NUMBER: A-42

ANALYTICAL METHOD: Instrumental Methods for Total Organic Carbon

ANALYTES: Organic carbon

DESCRIPTION: Organic carbon is determined by oxidation with infrared detection (2-200 mg/L range) or reduction with flame ionization detection (1-2000 mg/L range).

APPLICATIONS: Aqueous streams

GENERAL METHOD PARAMETERS:

Preparative Requirements: Preserve the H_2SO_4 to pH <2 and refrigerate to 4°C. Grab (S-11) or composite (S-10) samples may be analyzed using this method.

Method: Organic carbon in a sample is converted to carbon dioxide (CO_2) by catalytic combustion or wet chemical oxidation. The CO_2 formed can be measured directly by infrared detector or converted to methane (CH_4) and measured by a flame ionization detector. The amount of CO_2 or CH_4 is directly proportional to the concentration of carbonaceous material in the sample.

LIMITATIONS: Results may be influenced by sample handling prior or during the analysis. Organic carbon can be determined by difference between the total and inorganic carbon or by analysis of an acidified sparged sample. Sparging may result in a loss of volatile components. Analysis of samples with a high inorganic carbon content for low level TOC by difference may result in poor accuracy and precision. Filtration of the sample prior to analysis will limit the determination to soluble or dissolved organic carbon.

METHOD NUMBER: A-42

SENSITIVITY: 0.1 to 10 mg/L.

QA/QC: Calibration standards are prepared and analyzed in order to generate a calibration curve. Blanks, calibration standards, blank spikes, matrix spikes, and matrix replicates should be analyzed with each sample set. The recovery and precision of analysis should be reported.

EXTERNAL COST:

Per single analysis	\$15-\$35

INTERNAL COST:

Manhours/analysis	0.1-0.2
Capital Equipment:	
Total Organic Carbon Analyzer	\$10,000-\$25,000

PRIMARY REFERENCES: USEPA. Proposed Rules. Federal Register, 44(233), December 3, 1979. [Amendment to 40 CFR 136]

American Society for Testing and Materials. Annual Book of ASTM Standards, Part 31. Philadelphia, Pennsylvania, 1975. [Method D-2579 - Tests for Total and Organic Carbon in Water]

METHOD NUMBER: A-42

USEPA, Office of Technology Transfer, Methods for Chemical Analysis of Water and Wastes, EPA 625/6-74-003, Washington, D.C., 1974, p. 236. [NTIS No. PB 297686/AS]

American Public Health Association, American Water Works Association, and Water Pollution Control Federation. Standard Methods for the Examination of Water and Wastewater, 14th Edition. APHA, Washington, D.C., 1976, p. 532. [Method 505]

METHOD NUMBER: A-43

ANALYTICAL METHOD: Infrared Analysis for Inorganic Carbon

ANALYTES: Total inorganic carbon

DESCRIPTION: Evolved CO_2 is measured by non-dispersive infrared.

APPLICATIONS: Samples with high levels of dissolved carbonate/bicarbonate will require dilution. Grab (S-11) or composite (S-10) samples may be analyzed using this method.

GENERAL METHOD PARAMETERS:

Preparative Requirements: Sample should be homogeneous, and stored in glass at 4°C.

Method: Inorganic carbonates are decomposed with acid and sparged as carbon dioxide. The carbon dioxide evolved is measured with a non-dispersive infrared analyzer (NDIR). Filtration prior to analysis limits the results to soluble inorganic carbon.

LIMITATIONS: Volatile organic carbon may be purged and interfere with the determination.

SENSITIVITY: 0.1 - 100 mg/L.

QA/QC: Calibration standards are prepared and analyzed in order to generate a calibration curve. Blanks and matrix replicates should be analyzed with each sample set. The precision of analysis should be reported.

METHOD NUMBER: A-43

INTERNAL COST:

Manhours/analysis	0.1-0.3
Capital Equipment:	
Total carbon analyzer	$10,000-$25,000

REFERENCE: American Society for Testing and Materials. Annual Book of ASTM Standards, Part 31, 1975. [Method 505 - Total and Organic Carbon in Water].

METHOD NUMBER: A-44

ANALYTICAL METHOD: Membrane Electrode Measurement

ANALYTES: Dissolved oxygen content

DESCRIPTION: An oxygen sensitive electrode is immersed in the sample. The diffusion current measured is directly proportional to the molecular oxygen concentration.

APPLICATIONS: Any aqueous sample. Highly colored or heavily polluted waters may also be analyzed with this technique.

GENERAL METHOD PARAMETERS:

Method: The membrane electrode is calibrated against a water sample of known dissolved oxygen concentration (as determined by the iodometric method), and a blank with no dissolved oxygen (excess sodium sulfite and trace $CoCl_2$ will bring the dissolved oxygen content to zero). The electrode is then calibrated for the type of aqueous sample to be measured, i.e., fresh, salt, estuary, etc., water. The dissolved oxygen content of the sample is measured with the calibrated membrane electrode and reported.

LIMITATIONS: Electrodes generally exhibit high temperature coefficients due to membrane permeability changes.

SENSITIVITY: Usually to ± 0.1 mg/L.

QA/QC: Calibration standards are prepared and analyzed in order to generate a calibration curve. Blanks, calibration standards and matrix replicates should be analyzed with each sample set. The precision of analysis should be reported. Temperature correction is required.

EXTERNAL COST:

Per single analysis	$10-$25

INTERNAL COST:

Manhours/analysis	0.1-0.2
Capital Equipment:	
Dissolved oxygen electrode, meter	$500-$1,500

REFERENCES: American Public Health Association, American Water Works Association, and Water Pollution Control Federation. Standard Methods for the Examination of Water and Wastewater, 14th Edition. Washington, D.C., 1976. [Method 422 - Oxygen Dissolved]

USEPA, Office of Technology Transfer, Methods for Chemical Analysis of Water and Wastes, EPA 625/6-74-003, Washington, D.C., 1974, p. 51.

American Society for Testing and Materials, Annual Book of ASTM Standards, Part 31. Philadelphia, Pennsylvania, 1975. [Method D-1589]

METHOD NUMBER: A-45

ANALYTICAL METHOD: Ion Chromatography

ANALYTES: Ionic Species, i.e., Sulfate, Chloride, Formate

DESCRIPTION: The aqueous sample is directly injected onto an ion exchange column. The eluent, which may be varied in ionic strength or composition for a specific analyte, flows through the column and the ionic species eluted are quantified by a conductivity detector. Chemical red-ox potential detection is also available. Various exchange resins and suppressor column options are available for specific analysis needs.

APPLICATIONS: Aqueous samples or aqueous extracts of solids may be analyzed.

GENERAL METHOD PARAMETERS:

Method: IC may be used for determination of F^-, Cl^-, NO_2^-, NO_3^-, $SO_3^{=}$, $SO_4^{=}$, and $PO_4^{\equiv}$ in bulk aqueous liquids and also in the solution resulting from the aqueous extraction of bulk solids.

A solution of distilled, deionized water containing 0.5 g each of $NaHCO_3$ and Na_2CO_3 per liter is used as the eluent. The sample is first filtered and then injected into a sample loop (typically 1 to 2 mL must be injected; 0.1 mL to fill the sample loop and the remainder to fill the tubing leading to the sample loop). A pump rate of approximately 1.5 mL/min (300-400 psig) is used. The anions elute in the following order: F^-, Cl^-, NO_2^-, NO_3^-, $PO_4^{\equiv}$, $SO_3^{=}$, and $SO_4^{=}$. (Br^- will also elute if present.) The anions of interest are then determined by either the method of standard additions or by use of a calibration curve. The method of standard additions should be used whenever the presence of interferences is suspected. These include polyvalent cations such as Fe^{+3} and Al^{+3}, which interfere by forming complexes with F^-; and iron, which will interfere with $PO_4^{\equiv}$ and Cl^- through complex formation.

LIMITATIONS: Species which are unstable or have low ionic strength are difficult to analyze. Complex species do not elute well. Some suppressor columns require regeneration after a period of usage.

SENSITIVITY: 0.1-10 mg/L depending on column and analyte.

QA/QC: Calibration standards are prepared and analyzed in order to generate a calibration curve. Blanks, calibration standards, blank spikes, matrix spikes and matrix replicates should be analyzed with each sample set. The precision and recovery of analysis should be reported. Columns must be regenerated frequently.

EXTERNAL COST:

Per single analysis	\$10-\$60 (depending on analytes and sample matrix)

INTERNAL COST:

Manhours/analysis	0.1-1 (depending on analytes and sample matrix)
Capital Equipment:	
Ion Chromatograph	\$15,000-\$25,000

REFERENCES: Fritz, J.S., D.T. Gjerde, and C. Pohlandt. Ion Chromatography. Huthig Verlag. Heidelberg, New York, 1982.

Small, H., T.S. Stevens, and W.C. Baumar, "Novel Ion Exchange Chromatographic Method Using Conductimetric Detection," Anal. Chem., 47, 1801-1809, 1975.

Lentzen, D.E., D.E. Wagoner, E.D. Estes, and W.F. Gutknecht. EPA/IERL-RTP Procedures Manual: Level 1 Environmental Assessment, Second Edition. EPA Research Triangle Park, NC, 27709. EPA-600/7-78-201, 1978.

METHOD NUMBER: A-46

ANALYTICAL METHOD: Sedimentation

ANALYTES: Settleable Solids

DESCRIPTION: Solids are measured volumetrically in an Imhoff cone.

APPLICATIONS: All aqueous samples.

GENERAL METHOD PARAMETERS:

Preparative Requirements: Samples cannot be altered or preserved chemically. Grab samples (S-11) may be more appropriate for determination if sedimentation occurs over long compositing periods.

Method: An Imhoff cone is filled to the liter mark with a thoroughly mixed sample. The sample is allowed to settle for 45 minutes, and gently stirred with a rod or by spinning and allowed to settle 15 minutes longer. The volume of seattleable material is recorded as milliliters per liter.

LIMITATIONS: Floatable material, if present, is not measured. For some applications, suspended solids (A-2) which measures both seattleable and floatable material, may be preferred.

SENSITIVITY: Practical lower level is ∿1 mL/L/hr.

EXTERNAL COST:

Per single analysis	\$10-\$30

METHOD NUMBER: A-46

INTERNAL COST:

Manhours/analysis	0.2-1
Capital Equipment:	
Imhoff cones	$20-$50

REFERENCES: USEPA, Office of Technology Transfer, Methods for Chemical Analysis of Water and Wastes, EPA-625/6-74-003, Washington, D.C., 1974, p. 273.

American Public Health Association, American Water Works Association and Water Pollution Control Federation. Standard Methods for the Examination of Water and Wastewater, 14th edition. Washington, D.C., 1976 [Method 213].

METHOD NUMBER: T-01

TEST METHOD: Laboratory Corrosion Testing of Metals

DESCRIPTION: The corrosivity of wastes may be determined by pH measurement (H_2O)or corrosion of steel. A waste is considered to be corrosive, as defined by RCRA, 40 C.F.R. Part 261.22 if it is aqueous and has a pH ≤ 2 or ≥ 12.5; or it is liquid and corrodes steel at a rate >6.35 mm per year at a test temperature of 55°C.

APPLICATIONS: This technique is applicable to solid streams that contain a liquid fraction, including organic streams.

GENERAL METHOD PARAMETERS:

Preparative Requirements: The liquid fraction of the solid waste stream must be separated from solids for use in this test. Centrifugation, filtration, or settling may be used as the separatory method.

Method:

Corrosivity Toward Steel - The weight loss of a circular coupon of SAE type 1020 steel is determined after a designated time period (200-2,000 hours). The waste must be agitated and maintained at 55°C throughout the duration of exposure. The coupon must be carefully cleansed prior to each weighing.

LIMITATIONS: Large differences in corrosion rates occasionally occur under conditions where the metal surface becomes passivated.

SENSITIVITY: Corrosion rates of duplicate coupons are reproducible only to within 10%.

QA/QC: Samples should be analyzed in duplicate. The precision of analysis should be reported.

EXTERNAL COST:

Per single analysis	$50-$200

INTERNAL COST:

Manhours/Analyses	4-8
Capital Equipment:	
Reflux Condenser, Coupons Specimen Mounting Racks	$500-$1,500

REFERENCES: U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. "Test Methods for Evaluating Solid Wastes"--Physical/Chemical Methods. SW-846, Washington, DC, July 1982. (Method 1110 - Based on NACE Standard TM-01-69, 1972 Revision.)

METHOD NUMBER: T-02

TEST METHOD: Reactivity (RCRA)

DESCRIPTION: The RCRA classification scheme for reactivity includes six categories: (1) undergoes violent change without detonating, (2) reacts violently with water, (3) forms explosive mixtures with water, (4) generates toxic gases when mixed with water, (5) cyanide and sulfide-bearing waste (pH 2-12.5) which generates fumes or gases, and (6) wastes capable of detonation when heated or confined. If a waste can be assigned to any of these categories on the basis of qualitative or quantitative test results, it is classified as hazardous. Although test methods are not specified by EPA in the reference given, analytical methods for HCN (A-28) and H_2S (A-29) are available and a number of ASTM methods for explosivity and detonation characteristics appear applicable (see references).

APPLICATIONS: This technique is applicable to streams expected to be reactive in the exact manner(s) listed above (sublimating solids, H_2S and CN-containing streams, tars containing volatile organics).

GENERAL METHOD PARAMETERS:

Preparative Requirements: The sample should be representative of the waste and maintained without chemicals. Technique is applicable for all types of random and composite samples (S-01).

SENSITIVITY: The reactivity classification is assigned on the basis of qualitative judgements.

QA/QC: Does not apply unless specific tests for explosivity, CN^-, and H_2S are performed

EXTERNAL COST:

Per single analysis	\$10-\$250

INTERNAL COST:

Manhours/Analyses	0.5-8
Capital Equipment:	
Explosion Tester	\$100-\$250
CN^- Distillation Equipment	\$100-\$500

REFERENCES: U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. Test Methods for Evaluating Solid Wastes-Physical/Chemical Methods. SW-846. July 1982. [Methods 9010 (CN^-) and 9030 (H_2S) from same document]

USEPA. Rules and Regulations. Federal Register, 45(98), May 19, 1980. [Hazardous Waste Management System]

American Society for Testing and Materials, Philadelphia, Pennsylvania, Annual Book of ASTM Standards, Part 25 [Method D3115 - Test for Explosive Reactivity of Lubricants with Aerospace Alloys Under High Shear, Method D2389 - Test for Minimum Pressure for Vapor Phase Ignition of Monopropellants, Method D2539 - Test for Shock Sensitivity of Liquid Monopropellants by the Card Gap Test], and Part 41, [Method E680 - Test for Drop Weight Impact Sensitivity of Solid-Phase Hazardous Materials].

TEST METHOD: Pensky-Martens Closed-Cup Method for Ignitability of Solids

DESCRIPTION: Solid sample is heated at a slow constant rate with continual stirring while a small flame is directed into cup at regular intervals and the flash point is determined.

APPLICATIONS: This technique is applicable only to streams expected to be ignitable (e.g., organic sludges, tars, and resins); it does not apply to solids which have been exposed to high temperature or combustion; i.e., ashes or slags.

GENERAL METHOD PARAMETERS:

Preparative Requirements: Samples are stored in glass containers since volatile materials may diffuse through the walls of plastics bottles. This technique is applicable to random or composite samples (S-01). Approximately 50 mL of sample is used per test.

Method: The sample is heated at a rate sufficient to achieve a constant 5-6°C/minute increase in temperature. For samples with flash points below 110°C the flame is directed into the cup at 1°C intervals starting at a temperature 15 to 30°C less than anticipated flash point. For samples with flash points over 110°C, the flame is directed into the cup at 2°C intervals starting at a temperature 15 to 30°C less than the anticipated flash point.

LIMITATIONS: Ambient pressures, sample homogeneity, drafts, and operator bias can affect flash point values.

SENSITIVITY: Sensitivity will depend on thermometer accuracy, barometer accuracy, purity of reference standards, and operator precision.

QA/QC: Duplicates and standard reference materials should be routinely analyzed. The flash point of the p-xylene standard must be determined in duplicate at least once per sample batch; the average of the two analyses should be 27° ± 0.8°C.

EXTERNAL COST:

Per single analysis	\$10-\$60

INTERNAL COST:

Manhours/Analyses	0.2-1
Capital Equipment:	
Pensky-Martens Cup	\$700-\$1200

REFERENCES: USEPA, Office of Solid Waste and Emergency Response. Test Methods for Evaluating Solid Wastes Physical/Chemical Methods. SW-846. July 1982. [Method 1010, (Based on ASTM D93-77)].

USEPA. Rules and Regulations. Federal Register, 45(98), May 19, 1980. [Hazardous Waste Management System]

American Society for Testing and Materials, Philadelphia, Pennsylvania, Annual Book of ASTM Standards, Parts 15, 22, 23, 27, and 29 [Method D93 - Test for Flash Point by Pensky-Martens Closed Tester]

METHOD NUMBER: T-04

TEST METHOD: Permeability (Hydraulic Conductivity) of Solid Waste Samples

DESCRIPTION: The waste is mixed with water at optimum moisture content and compacted into the permeameter. The rate of leachate production is monitored. Permeability coefficients are calculated from the amount of leachate collected and the hydraulic gradient applied.

APPLICATIONS: This technique is applicable only to the solid fraction of solid waste streams. It is inappropriate for water soluble solids.

GENERAL METHOD PARAMETERS:

Preparative Requirements: Technique is applicable for all types of random or composite samples (S-01). A minimum of 5 lb of sample is required. Sample should be representative of the waste, and care should be taken to maintain the physical integrity of the specimen. The sample should not be subjected to grinding or other processes that could modify the particle size distribution.

Method: A portion of the sample is compacted in a permeameter. The apparatus is evacuated for 15 minutes. Evacuation is followed by slow saturation of the sample with water from the bottom upward, then is slowly allowed to saturate with water from the bottom up under full vacuum. The vacuum is disconnected and the quantity of flow from the saturated sample is determined under various conditions of applied hydraulic head. The permeability coefficient is calculated from the resulting data.

LIMITATIONS: If material is either extremely permeable or extremely impermeable, accurate measurements will be difficult to achieve. If material reacts with water, or gases are formed, measurements will be adversely affected.

METHOD NUMBER: T-04

SENSITIVITY: The applicable range of the method is between 10^{-3} and 10^{-8} cm/sec; method is imprecise outside these boundaries.

QA/QC: A minimum of one column should be run in duplicate per batch of measured mixtures. Gas regulators should be checked regularly.

EXTERNAL COST:

Per single analysis	$50-$500

INTERNAL COST:

Manhours/Analyses	4-24
Capital Equipment:	
Permeameter	$50-$250

REFERENCES: Department of Army Office of Chief of Engineers. Laboratory Soils Testing, Engineer Manual, EM 1110-2-1906, Appendix VII. Headquarters, 1970.

American Society for Testing and Materials, Philadelphia, Pennsylvania, Annual Book of ASTM Standards, Part 19 [Method D2434 - Test for Permeability of Granular Soils (Constant Head)]

METHOD NUMBER: T-05

TEST METHOD: Particle-Size Distribution of Solid Samples

DESCRIPTION: A quantitative distribution of sizes larger than 75 microns is determined by sieving, while particle sizes smaller than 75 microns can be determined by a sedimentation process using a hydrometer.

APPLICATIONS: This technique is applicable to any solid waste stream which has a soil-like consistency and does not react with water. It can usually be applied successfully to ashes, slags, and some sludges,but not to tars.

GENERAL METHOD PARAMETERS:

Preparative Requirements: The sample should be representative of the waste, and it should not contain preservatives. Grab or composite (S-01) samples may be analyzed using this technique.

Method:

Sedimentation - The sedimentation rate of a mixture, the sample, a surfactant and distilled water, is determined at a constant temperature with a hydrometer. The particle size is calculated from the resulting data.

LIMITATIONS: Samples must be dried and free-flowing. If drying causes particle-size abberation through aggregate formation, measurement will be imprecise. Samples that react or are highly soluble with water cannot be successfully subjected to this method.

SENSITIVITY: There is not an established standard limit of acceptable sensitivity for this method.

QA/QC: At least one duplicate particle-size analysis per sample batch should be performed.

EXTERNAL COST:

Per single analysis	$50-$200

INTERNAL COST:

Manhours/Analyses	2-4
Capital Equipment:	
Sieve Set	$1,000-$2,000
Rotovap	$500-$2,000
Hydrometer	$50-$200

REFERENCES: American Society for Testing and Materials, Philadelphia, Pennsylvania, Annual Book of ASTM Standards, Part 19 [Method D422 - Particle-Size Analysis of Soils] and Part 26 [Method D410 - Sieve Analysis of Coal, and Method D431 - Designating the Size of Coal from its Sieve Analysis]

TEST NUMBER: T-06

TEST METHOD: Specific Gravity of Solid Samples

DESCRIPTION: Several methods may be used to determine the volume, a specific (unit) mass of waste will occupy when voids are excluded.

APPLICATIONS: The specific gravity of every solid waste stream can be determined, but the method will be different for streams with different physical/chemical properties. The references listed should be consulted to select a procedure for a specific waste stream.

GENERAL METHOD PARAMETERS:

Preparative Requirements: Samples should be as representative and as homogeneous as possible. No preservatives should be added unless required by the procedure.

Method: In some cases, a sample can simply be dried, weighed, and submerged under a liquid to determine volume displacement; in other instances it will be necessary to coat the solids with paraffin, or use a pycnometer with special procedures.

LIMITATIONS: For certain wastes with mixed character no single method will be perfect for specific gravity determination. Waste inhomogeneity can cause results to vary.

SENSITIVITY: The sensitivity for each method is specified in the references.

QA/QC: Matrix replicates should be analyzed with each sample set. The precision of analysis should be reported.

METHOD NUMBER: T-06

EXTERNAL COST:

Per single analysis	$25-$500 (depending on specific procedure required)

INTERNAL COST:

Manhours/Analysis	2-8 (depending on specific procedure required)
Capital Equipment:	
Hogarth Specific Gravity Bottle	$50-$100
Pycnometer	$50-$500

REFERENCES: American Society for Testing and Materials, Philadelphia, Pennsylvania, Annual Book of ASTM Standards, Parts 15 and 19 [Method D70 - Test for Specific Gravity of Semi-Solid Bituminous Materials, Method D1188 - Test for Bulk Specific Gravity of Comparted Bituminous Mixtures Using Paraffin-Coated Specimens] and Part 19 [Method C97 - Tests for Absorption and Bulk Specific Gravity of Natural Building Stone, Method 854 - Test for Specific Gravity of Soils]

METHOD NUMBER: T-07

TEST METHOD: In-Place Bulk Density of Solids

DESCRIPTION: A sand cone method and/or balloon densitometer are used to obtain a known weight of damp solid sample from a representative irregular hole in the solid waste pile. The volume of the hole and the percent moisture of the wastes are determined. The volume occupied by a given mass of waste under normal in-place conditions is calculated.

APPLICATIONS: This technique is applicable to solid waste streams having a soil-like consistency (ashes, slags, and dewatered sludges) that are placed in piles before final disposal.

GENERAL METHOD PARAMETERS:

Sand Cone Method: This method is restricted to tests in soils containing particles not larger than 2 inches in diameter.

Rubber Balloon Method: This method covers the determination of the density in-place of compacted or firmly bonded soil. It is not suitable for very soft material which will deform under slight pressure. For such materials the sand cone method may be used.

LIMITATIONS: In-place bulk density measurements can vary due to waste pile inhomogeneity. Representative samples must be taken from several areas of the pile.

SENSITIVITY: With careful instrument calibration, the method can be both precise and accurate.

QA/QC: Field-density test apparatus should be calibrated regularly and duplicate measurements performed in similar site areas.

METHOD NUMBER: T-07

EXTERNAL COST:

Per single analysis	$10-$100

INTERNAL COST:

Manhours/Analysis	1-2
Capital Equipment:	
Sand Cone Apparatus	$25-$300
Balloon-Density Apparatus	$100-$500

REFERENCES: American Society for Testing and Materials, Philadelphia, Pennsylvania, Annual Book of ASTM Standards, Part 19, [Methods D1556 - Test for Density of Soil in Place by the Sand-Cone Method, Method 2167 - Test for Density of Soil in Place by the Rubber-Balloon Method]

American Association of State Highway Officials. Standard Specifications for Transportation Materials and Methods of Sampling and Testing, 11th Edition, Washington, D. C., 1974.

METHOD NUMBER: T-08

TEST METHOD: Moisture-Density Relations of Solids (Optimum Moisture at Maximum Dry Bulk Density)

DESCRIPTION: At least four representative samples of waste are prepared by adding increasing amounts of water to each sample and compacting into a standard compaction mold. A plot of moisture versus density usually forms a parabola in which the optimum moisture content corresponds to the maximum dry density.

APPLICATIONS: This technique is applicable to any solid waste stream having a soil-like consistency. While it is appropriate for ashes, slags, and dewatered sludges, it cannot be used effectively with tars and resins.

GENERAL METHOD PARAMETERS:

Preparative Requirements: The sample should be representative of the waste, and should not have preservatives added to it. The original moisture content should be maintained as practicable. Grab or composite samples (S01) may be analyzed using this technique. Approximately 2kg is required.

Method: A portion of the sample is sieved to a uniform particle size and mixed with water. The sample is then uniformly compacted to a known volume and the weight of the sample determined. A representative portion is weighed, dried, and reweighed and the weight of water determined. This procedure is repeated until a constant weight is obtained. The resulting data is used to determine the moisture density relation.

LIMITATIONS: For free-draining aggregate mixtures, a well-defined moisture-density relationship cannot be produced.

METHOD NUMBER: T-08

SENSITIVITY: The acceptable range of relative standard deviation (ASTM) for maximum density and optimum moisture content for soil-like materials are ±1.66 and ±0.86, respectively.

QA/QC: At least one point per compaction curve near the maximum should be duplicated.

EXTERNAL COST:

Per single analysis	\$60-\$250

INTERNAL COST:

Manhours/Analyses	4-8
Capital Equipment:	
Compaction Mold	\$100-\$300
Rammer	\$100-\$200 (Manual) \$5,000-\$10,000 (Automated)
Extruder	\$50-\$100

REFERENCES: American Society for Testing and Materials, Philadelphia, Pennsylvania, Annual Book of ASTM Standards, Parts 14, 15 and 19, [Methods D698-78, C127, D854, D2168, D2216, D2487, D2488, E11, and D1557-78] Parts 13, 14, 15, 18, 20, 30 and 41 [Method E11 - Specifications for Wire-Cloth Sieves for Testing Purposes], Parts 14 and 15 [Method C127 - Test for Specific Gravity and Absorption of Coarse Aggregate], and Part 19 [Method D558 - Test for Moisture - Density Relation of Soil-Cement Mixtures, Method D698 - Tests for Moisture-Density Relations of Soils and Soil-Aggregate Mixtures, Method D854-Test for Specific Gravity of Soils, Method D1557 -

Tests for Moisture Density Relations of Soils and Soil-Aggregate Mixtures, Method D2168 - Calibration of Laboratory Mechanical-Panimer Soil Compactors, Method D2216 - Laboratory Determination of Water (Moisture) Content of Soil-Rock and Soil Aggregate Mixtures, Method D2487 - Classification of Soils for Engineering Purposes]

METHOD NUMBER: T-09

TEST METHOD: Specific Conductance (Conductivity) of Aqueous Samples

DESCRIPTION: Specific conductance is measured using a conductivity meter.

APPLICATIONS: All wastewater streams including those from organic and organic-free sources.

GENERAL METHOD PARAMETERS:

Preparative Requirements: Samples are kept cool (4°C) if analysis cannot be performed within 24 hours. Grab (S11) or composite (S10) samples may be analyzed using this technique.

Method: The specific conductance of a sample is measured with a self-contained conductivity meter (Wheatstone bridge-type or equivalent.) Samples are analyzed at 25°C or temperature corrections are made and results are reported at 25°C.

SENSITIVITY: 10-50 μmhos/cm at 25°C.

QA/QC: KCl standard solution analyses are performed daily for instrument calibration.

EXTERNAL COST:

Per single analysis	\$5-\$15

INTERNAL COST:

Manhours/Analysis	~0.1

METHOD NUMBER: T-09

Capital Equipment:

Conductivity Meter	$300-$1,500

REFERENCES: USEPA. Proposed Rules. Federal Register, 44(233), December 3, 1979. [Amendment to 40 CFR 136]

American Society for Testing and Materials, Philadelphia, Pennsylvania, Annual Book of ASTM Standards, Part 31 [Method D1125 - Tests for Electrical Conductivity and Resistivity of Water]

USEPA. Office of Technology Transfer, Methods for Chemical Analysis of Water and Wastes, EPA-625/6-74-003, Washington, D. C., 1974. NTIS No. PB 297686/AS p. 275.

American Public Health Assoc., American Water Works Assoc., and Water Pollution Control Federation. Standard Methods for the Examination of Water and Wastewater, 14th edition. APHA, Washington, D. C., 1976. pp. 75. [Method 205]

METHOD NUMBER: T-10

TEST METHOD: Viscosity (Fluid Friction) Determination in Liquids, Tars, and Sludges

DESCRIPTION: Fluid friction is measured by different methods for liquids, tars, and sludges.

APPLICATIONS: Viscosity measurements are applicable only to fluid solids streams which contain a liquid fraction.

GENERAL METHOD PARAMETERS:

Preparative Requirements: Technique will vary with method. Special attention must be given to stratified streams.

Method: For liquids, the resistive flow of a fluid under gravity can be measured through a capillary of a calibrated viscometer under a reproducible driving head at controlled temperature. For asphalt and tar-like samples, a sliding plate microviscometer is used to measure the ratio between the applied shear stress and the rate of shear. An insertable Brookfield viscometer is used for high-solids sludges.

LIMITATIONS: Limitations for given methods are discussed in references. The major limitation is providing a representative sample.

SENSITIVITY: Sensitivity of measurement is procedure- and waste-dependent.

QA/QC: Equipment is calibrated and matrix replicates analyzed as given in the references.

METHOD NUMBER: T-10

EXTERNAL COST:

Per single analysis	$20-$300 (depending on procedure required)

INTERNAL COST:

Manhours/Analysis	1-10 (depending on procedure required)

Capital Equipment:

Brookfield Viscometer	$300-$1,000
Capillary Viscometers	$100-$500
Capillary Viscometer Bath	$1,500-$2,500
Sliding Plate Microviscometers	$100-$500

REFERENCES: American Society for Testing and Materials, Philadelphia, Pennsylvania, Annual Book of ASTM Standards, Parts 10, 14, 32, 35, and 51 [Method E4], Part 15 [Methods D5, D2170, D2171, D3205, and D3570], Parts 15, 22, 23, 27, and 29 [Method D93], Parts 15, 23, and 40 [Method D92], Parts 23 and 40 [Method D445], Part 23 [Method D446], and Parts 25 and 44 [Method C1]

Brookfield Viscometer Manual for Operators

METHOD NUMBER: T-11

TEST METHOD: Determination of Specific Surface Area of Solids

DESCRIPTION: The specific surface refers to the area per unit weight of waste usually in m^2/g. There are a number of absolute and relative methods which yield total surface area (including the area associated with pores): the Harkins-Jura absolute method, gas adsorption (BET), liquid adsorption, and mercury porosimetry. See Table 1 for discussion of principles.

APPLICATIONS: Surface area can be determined only on solid, dry samples (e.g., ash, slag, dewatered sludge).

LIMITATIONS: Each type of surface area method has certain limits, e.g., absolute methods must have a firm theoretical basis for application and experimental conditions must be precisely controlled for relative methods. All methods require a representative homogeneous sample. See Table 1 for further discussion about specific methods.

SENSITIVITY: Most absolute methods for surface area determination are highly precise, but not always accurate. Relative methods may be imprecise. (See Table 1.)

QA/QC: Control measures should include those normally used with a specific method.

SAMPLING/SAMPLE HANDLING REQUIREMENTS: A representative, dry solid sample should be taken for this analysis. Care should be taken to avoid surface manipulation (i.e., no breaking or grinding should be performed).

EXTERNAL COST:

Per single analysis	\$200-\$1,000 (depending on procedure)

TABLE 1. METHODS FOR DETERMINATION OF SPECIFIC SURFACE AREA

Method	Principle	Equipment	Limitations	Precision and Accuracy
Harkins-Jura Absolute Method	Calorimetric determination of energy change when suspended particles are dropped from saturated vapor into bulk liquid.	Precision calorimeter, analytical balance	Too involved for routine work.	Absolute method used as standard for evaluating other methods.
Gas Adsorption (BET)	Measures volume of adsorbed inert gas required to form a monolayer.	BET apparatus (vacuum degassing, pressure, and temperature measurements)	Tedious, time consuming.	Can be used to measure specific surface area down to 100 cm^2/g. Conventional technique gives 2-4% reproducibility. Simplified methods give 10-20%.
Liquid Adsorption	Measures amount of liquid component (sorbate) adsorbed from a solvent on solid surface.	Flask, shaker, equipment for analysis of sorbate concentration	Applicability of a specific solid/liquid/sorbent system must be determined experimentally. Time required to reach equilibrium varies.	Accuracy is determined by comparison with other methods (BET). Reproducibility is within 5%.

METHOD NUMBER: T-11

INTERNAL COST:

Manhours/analyses	2-8 (depending on procedure)

Capital Equipment:

BET analyzer	$10,000-$20,000

REFERENCES: Mortland, M. M., and W. D. Kemper, Specific Surface, Methods of Soil Analysis, American Society of Agronomy, 1965, pp. 532-546.

Schwitzgebel, K., Meserole, F. M., Thompson, C. M., Skloss, J. L., and N.P. Phillips, "Development of Sampling and Analytical Methods of Lime/Limestone Wet Scrubbing Tests," Vol. I and II, Final Report, OAP Contract No. CPA 70-143, Radian Project No. 200-006.

METHOD NUMBER: T-12

TEST METHOD: Bioassay for Health Effects

DESCRIPTION: A variety of test organisms are exposed to a prepared sample. After exposure, organisms are assayed for symptoms of adverse effects. Common screening organisms are given in Table 1.

APPLICATIONS: Liquids, solids, condensed gases and extracts of all three media may be assayed for mutagenicity, cytotoxicity or acute toxicity.

LIMITATIONS: Screening test results may be difficult to interpret or assign to a specific component of the sample. Interpretation must be performed by an experienced professional.

SENSITIVITY: Test species are selected for their sensitivity to respond. Response quantifiable in most cases.

QA/QC: Dose response and multiple trials should be conducted. Good biological laboratory practices are mandatory.

EXTERNAL COST:

Per single analysis	$400-$2,000

INTERNAL COST:

Manhours/analysis	1-40

Capital Equipment:

Cell culture assembly	$1,000-$6,000
Animal housing	$3,000-$10,000

TABLE 1. GENERAL HEALTH EFFECTS BIOASSAY TESTS

Test Designation/ Assay Type	Activity Measured	Test Organism	Appropriate Sample Type
Ames/in-vitro	Mutagenesis (point mutation)	Salmonella Typhimurium	Liquids, extracts of solids particles
RAM/in-vitro	Cytotoxicity, EC_{50}	Rabbit Alveolar Macrophage	Particles
CHO/in-vitro	Cytotoxicity, EC_{50}	Chinese Hamster Ovary	Liquids, extracts
CHO/K1/in-vitro	Mutagenesis (point mutation)	Chinese Hamster Ovary	Liquids, extracts
CHO/SCE/in-vitro	Mutagenesis (gross genetic change)	Chinese Hamster Ovary	Liquids, extracts

REFERENCES: D.J. Brusick and R.R. Young, IERL-RTP Procedures Manual: Level 1 Environmental Assessment Biological Tests, EPA 600/8-81-024.

D.J. Brusick and R.R. Young, Level 1 Bioassay Sensitivity, EPA 600/7-81-135.

Ames, B., J. McCann, and E. Yamasaki, Methods for Detecting Carcinogens and Mutagens with the Salmonella/Mammalian-Microsome Mutagenicity Test, Mutation Res., Vol. 31, 1975, pp. 347-364.

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Balazs, T., Measurement of Acute Toxicity, in Methods in Toxicology, G. Paget, Ed., F.A. Davis Co., Philadelphia, PA, 1970, pp. 49-81.

N.G. Sexton, Biological Screening of Complex Samples from Industrial/ Energy Processes, EPA 600/8-79-021.

METHOD NUMBER: T-13

TEST METHOD: Bioassay Testing for Ecological Effects

DESCRIPTION: A variety of test organisms are exposed to a sample or aqueous leachate of a sample. The test organisms are then assayed for signs or symptoms of ecological effects. Some generally used test species and the activities measured are given in Table 1.

APPLICATIONS: Numerous emission streams or extracts (leachates) of emission streams may be assayed. A variety of test species can be used.

LIMITATIONS: Test results are often difficult to associate with specific causes. Must be performed by an experienced professional.

SENSITIVITY: The test organisms commonly used are selected for their sensitivity to change within their environment and subsequent response.

QA/QC: Good biological laboratory practices are essential. Dose response and multiple assays are necessary to produce quality data.

EXTERNAL COST:

Per single analysis	$300-$6,000 (depending on test)

INTERNAL COST:

Manhours/analysis	20-120 (depending on test)

Capital Equipment:

Tanks, test species, incubators	$15,000-$50,000 (depending on laboratory facilities)

TABLE 1. GENERAL ECOLOGICAL EFFECTS BIOASSAY TESTS

Test Designation/ Assay Type	Activity Measured	Test Organism	Appropriate Sample Type
Acute Static Bioassay/Vertebrate	Lethality, LC_{50}	Fresh water or marine minnow	Aqueous leaches of solids or particulates
Acute Static Bioassay/Invertebrate	Lethality, LC_{50}	Daphnia (fresh water) or mysid (marine)	
Algae Growth/Algae	Growth Inhibition, EC_{50} or Growth Stimulation, SC_{20}	*Selenasium capricornutum*, *Skeletonemer costatum*	

REFERENCES: D.J. Brusick and R.R. Young, IERL-RTP Procedures Manual: Level 1 Environmental Assessment Biological Tests, EPA 600/8-81-024.

Lentzen, D.D., D.E. Wagoner, E.D. Estes and W.F. Gutknecht, EPA/IERL-RTP Procedures Manual: Level 1 Environmental Assessment, Second Edition, EPA-600/7-78-201 (January 1979), NTIS No. PB 293795/AS.

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Brungs, W.A. and D.I. Mount, A Device for Continuous Treatment of Fish in Holding Chambers, Trans. Amer. Fish Soc., Vol. 96, 1967, pp. 55-57.

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METHOD NUMBER: T-14

TEST METHOD: Opacity Measurement

DESCRIPTION: The opacity of a plume may be estimated by a qualified observer or determined as a function of the change in attenuation of a light projected through the emission.

APPLICATIONS: Visual opacity determinations may be made of plumes from almost any source. Instrumental (transmissometer) determinations require a stack or duct geometry for implementation.

LIMITATIONS: Visual determinations can only be made under favorable ambient conditions. Poor visual contrast to the plume generally causes some positive error. Instrumental determinations must be performed across a representative portion of the emission.

SENSITIVITY: Visual determinations have been verified against standardized transmissometer readings to ±5%. Allowable instrumental error is <3%.

EXTERNAL COST:

Per single visual determination	\$30-\$80 (excluding any travel or associated expenses for certified personnel)

INTERNAL COST:

Manhours/Determination	~0.1 (excluding personnel certification)
Capital Equipment:	
Opacity Monitor	\$3,000-\$5,000

METHOD NUMBER: T-14

REFERENCES: USEPA. Title 40, Code of Federal Regulations, Part 60, Appendix A. December 5, 1980 [Method 9 - Visual Determination of the Opacity of Emissions from Stationary Sources]

USEPA. Title 40, Code of Federal Regulations, Part 60, Appendix B. December 5, 1980 [Performance Specification 1 - Performance specifications and specification test procedures for transmissometer systems for continuous measurement of the opacity of stack emissions].

USEPA. Proposed Rules. Federal Register, 45(224), November 18, 1980. [Method 22 - Visual Determination of Fugitive Emissions from Material Processing Sources]

APPENDIX B
STATISTICAL ISSUES

Statistical procedures and theory have been used in the approaches given in this manual for monitoring plan development. This Appendix presents some background and additional discussions of these statistical procedures.

B.1 DATA DISTRIBUTIONS

A common statistical approach involves modeling a set of data with a distribution function. The set of data here refers to the measurements made for a specific parameter at a specific plant location. Statistical distributions often used for environmental and operating data include the normal distribution (for symmetrically distributed measurements), the lognormal distribution (for skewed measurements), and the binomial distribution for qualitative data (e.g., parameters classified as present/not present). When these distributions are adequate for modeling a set of measurements, properties of the distributions can be used to evaluate alternative monitoring strategies and develop decision rules.

The normal distribution is the most widely used statistical distribution model for measurement data. The properties of the normal distribution have been extensively developed. The model results in a symmetric distribution of measurements about a mean value, u. About two-thirds of the measurements are within one standard deviation (σ) of the mean, 95 percent of the measurements are within two standard deviations of the mean, and 99.7 percent of the measured values are within three standard deviations of the mean.

The mean (u) of a normal distribution can be estimated using the sample average:

$$\overline{x} = \frac{\sum^{n} x}{n}$$

where a sample of n measurements (x) of the parameter is available. The standard deviation (σ) is estimated using the sample standard deviation:

$$s = \sqrt{\frac{\sum^{n}(x-\bar{x})^2}{n - 1}}$$

The lognormal distribution is one of the most commonly used distribution models for environmental data. The model includes only positive values and is skewed toward smaller values. A measurement (x) can be modeled by the lognormal distribution if the transformed value $y = \ln(x)$ can be modeled with a normal distribution.

For the two-parameter lognormal distribution, the mean of the distribution is:

$$\text{mean} = e^{u + 1/2\sigma^2}$$

and the standard deviation of the distribution is:

$$\text{standard deviation} = e^{u}\,[e^{\sigma^2}(e^{\sigma^2} - 1)]^{1/2}$$

where u and σ are the mean and standard deviation of the lognormal of the data.

Finney (Reference B-1) has developed efficient estimators of the mean (M) and standard deviation $(V)^{1/2}$ for a sample from a lognormal distribution:

$$M = e^{\bar{y}}g(S_y^2/2)$$

$$V = e^{2\bar{y}}\{g(2S_y^2) - g[(n-2)S_y^2/(n-1)]\}$$

where $\bar{y}$ = the average of $y = \ln(x)$, for the sample of n measurements,

S_y = standard deviation of the y values, and

$g(t)$ = specific series in t (see Reference B-1).

The binomial distribution can be used to model data in which a parameter is classified as either present or not present, but no measured value is determined. This situation may occur when a multi-component analytical method used to analyze a sample is capable of identifying which compounds are present, but not quantifying the compounds. Therefore the data for each parameter states whether the compound is present or not present in each sample analyzed. The statistic usually evaluated with the binomial model is the percent occurrence rate:

$$\hat{p} = \frac{\text{number of times parameter was found present}}{\text{number of samples analyzed for parameter}} \times 100$$

The standard deviation of $\hat{p}$ can be estimated using:

$$\hat{\sigma}_p = \sqrt{\frac{\hat{p}\ (100-\hat{p})}{n - 1}}$$

where n is the number of samples analyzed.

The normal, lognormal, and binomial distributions are used as models in this document. The normal model is applicable if the parameter of interest has measurements which are symmetrically distributed about a mean value. The concentration of the parameter should be such that non-detected values are not common. The lognormal distribution should be considered as a model when measurements are skewed toward positive values. The binomial model is applicable when data is not quantified (e.g., detect, nondetect).

If sufficient data are available to support alternative distribution models for a particular parameter, the alternative model can be used within the framework of this document. The various properties and decision criteria presented here for the normal and lognormal models should be developed for the alternative models of measurement data. The Poisson, multinormal, and negative-binomial distribution can be used as alternative models for qualitative data. A statistician should be consulted if these alternative models are used.

Another situation occurs with environmental measurements when some of the data are quantitative and some of the data are qualitative (e.g., less than detection limit). Data bases of this type can be modeled using mixed-distributions; i.e., mixtures of discrete and continuous distribution models. An example is the use of a mixture of a binomial and lognormal distribution to model fugitive hydrocarbon emission data from process sources (Reference B-2). A statistician should be consulted to develop decision rules for statistics of this type.

An alternative approach to the use of distribution models would be nonparametric (or distribution-free) statistics. When using nonparametric statistics, no assumptions about the precise form of the distribution of the parameters measurements are made. Decision rules can be based on criteria that do not depend on the exact form of the distribution. The focus is on order statistics (minimum, maximum, etc.) and percentiles (median, 95th percentile, etc.). Estimation problems, such as estimating the mean concentration of a parameter, are usually more difficult when using nonparametric statistics; but under certain conditions, estimation can be accomplished.

B.2 CONFIDENCE INTERVALS

A confidence interval is a set of end points about a sample statistic that is believed, with a specified degree of confidence, to include the population parameter. The width of the confidence interval gives an indication of how precisely a parameter mean (or other statistic) can be estimated from the sample data. Commonly used confidence levels are 90 percent, 95 percent, and 99 percent. The expected width of a confidence interval for the parameter of interest can be used as a guide to evaluating alternative sampling and testing strategies.

The confidence interval for the population mean can be computed as follows:

1) Normal Distribution Model: $\bar{x} \pm t_{\alpha,(n-1)} S/\sqrt{n}$

where $\bar{x}$ is the sample mean,
$t_{\alpha,(n-1)}$ is the tabulated t-statistic with confidence level $(1-\alpha)$,
S is the sample standard deviation, and
n is the sample size (number of measurements).

2) Lognormal Distribution Model:

$$\left[e^{\bar{y} \pm t_{\alpha,(n-1)} S/\sqrt{n}}\right] g(S^2/2)$$

where $\bar{y}$ is the mean of $y = \ln(x)$ for the n sample measurements x,
S is the standard deviation of the y values,
$t_{\alpha,(n-1)}$ is the tabulated t-statistic, and
$g(S^2/2)$ is the series described in Section B.1.

The standard deviation expressed as a percentage of the mean is called the coefficient of variation (CV):

$$CV\ (\%) = (S/\bar{x}) \times 100.$$

The CV can be used as a substitute for S in the confidence interval formula for the normal distribution. The confidence limits would then be expressed as percentages of the mean.

For the lognormal model:

$$CV\ (\%) = 100(e^{\sigma^2} - 1)^{1/2}$$

where σ is the standard deviation of $y = \ln(x)$.

Given the CV for a parameter, the standard deviation in the lognormal distribution can be estimated by:

$$S = \sqrt{\ln[1 - (CV/100)^2]}\ .$$

The confidence limits can then be expressed as percentages of the mean:

$$\text{upper limit} = [e^{t_{\alpha,(n-1)}(S/\sqrt{n})}]$$

$$\text{lower limit} = [1 - \frac{1}{e^{t_{\alpha,(n-1)}(S/\sqrt{n})}}]$$

These formulas were used to develop the confidence intervals for the lognormal model in Table 4-18.

For qualitative data, the binomial distribution model can be used to develop confidence intervals for the percentage, p (i.e., how often the parameter is detected in the sample). For large sample sizes and percentages (i.e., $n > 50$, $p > 0.10$) the following can be used to approximate the confidence interval for the population percentage, p:

$$p = \frac{Z_{\alpha}\sigma}{2}p$$

where p, and σ_p are as defined in Section B.1., and $Z_{\frac{\alpha}{2}}$ is the appropriate value from a standard normal table. Table B-1 gives confidence intervals for p for some of the sample sizes expected from Phase 1 testing.

TABLE B-1. 95% CONFIDENCE INTERVAL FOR p = PERCENTAGE OF SAMPLES WITH DETECTED LEVEL OF THE PARAMETER FOR SMALL VALUES OF p AND n

No. of Detected Values	Number of Samples Tested for Parameter (n)					
	4	6	12	24	52	365
0	(0, 60)	(0, 46)	(0, 27)	(0, 14)	(0, 7)	(0, 1)
1	(0, 80)	(0, 64)	(0, 39)	(0, 21)	(0, 10)	(0, 2)
2	(7, 93)	(4, 78)	(2, 49)	(1, 27)	(0, 13)	(0, 2)
3	(20, 99)	(12, 88)	(5, 58)	(2, 33)	(1, 16)	(0, 3)
4	(40, 100)	(22, 96)	(10, 65)	(4, 38)	(2, 19)	(0, 3)
5		(36, 100)	(15, 72)	(7, 42)	(3, 21)	(0, 4)
6		(54, 100)	(21, 79)	(10, 47)	(4, 23)	(0, 4)
8			(35, 90)	(15, 55)	(7, 28)	(1, 4)
10			(52, 98)	(22, 64)	(10, 33)	(1, 5)
12			(73, 100)	(29, 71)	(12, 37)	(2, 6)
14				(36, 78)	(16, 41)	(2, 7)
16				(44, 85)	(19, 45)	(2, 7)
20				(62, 96)	(25, 53)	(3, 9)
24				(85, 100)	(32, 61)	(4, 10)
30					(43, 71)	(6, 12)
40					(63, 87)	(8, 15)
50					(87, 100)	(10,17)

Confidence intervals can also be calculated for other statistics such as the standard deviation. A statistician should be consulted for these calculations. Also, if distributed models other than those discussed here are used, a statistician should be consulted to develop the appropriate estimating formulas and confidence interval procedures.

The confidence intervals discussed in this section do not consider inaccuracies (biases) in the measurement data. If the data is 50% low (e.g., a method with only a 50% average recovery was used), then the estimated mean and the confidence limits will be 50% low. Procedures to compensate for analytical bias (systematic errors) in developing the confidence intervals can be developed with the aid of a statistician. Biases in the measured methods do not directly impact the decision on sample size selection which is the primary use of the confidence interval in this document.

B.3 UPDATING PARAMETER ESTIMATES

The measurement data obtained in Phase 2 can be used to update the Phase 1 data base for each parameter measured in Phase 2. Note that if only indicator parameters are measured during Phase 2 testing, these will be the only parameters updated. Data obtained during periods when no shift in the baseline levels were indicated can be used to update the Phase 1 mean and standard deviation for the parameters.

For the normal distribution model the updated mean ($\bar{X}_u$) and standard deviation (S_u) would be:

$$\bar{X}_u = \frac{n\bar{X}_1 + m\bar{X}_2}{n + m}$$

$$S_u = \left[\frac{(n-1)S_1^2 + (m-1)S_2^2}{n + m - 2}\right]^{1/2}$$

where $\bar{X}_1$ and S_1 are the Phase 1 mean and standard deviation (based on n tests) and $\bar{X}_2$ and S_2 are the Phase 2 mean and standard deviation (based on m tests).

For a lognormal distribution model, the transformed statistics $\bar{y}$ and S_y would be updated using the above formulas for the normal distribution model, and then the updated values could be used in the lognormal distribution formula (Section B.1).

B.4 CORRELATION COEFFICIENT

The correlation coefficient, r, is a measure of the strength of a linear relationship between two variables (X and Y). The correlation coefficient is defined as

$$r_{xy} = \frac{\text{covariance }(X,Y)}{[(\text{Variance of }X)\ (\text{Variance of }Y)]^{1/2}}$$

From a sample of data (pairs of measurements) the correlation coefficient can be estimated using:

$$r_{xy} = \frac{\sum^{n}(X_i-\bar{X})\ (Y_i-\bar{Y})}{[\sum^{n}(X_i-\bar{X})^2]^{1/2}\ [\sum^{n}(Y_i-\bar{Y})^2]^{1/2}}$$

If the correlation coefficient is near zero, the variables are said to be uncorrelated, that is, unassociated with each other. If the correlation coefficient is near 1 (positive or minus) then the variables are considered highly correlated.

The statistical significance of various values of r is dependent on the sample size, n. The following table gives critical values for testing the correlation between two variables to see if it is statistically significant (different from zero) for typical sample sizes from Phase 1 testing:

Statistical Significance of Sample Correlation Coefficient

Sample Size (n)	95% Level	99% Level
4	0.95	0.98
6	0.73	0.88
12	0.50	0.66
24	0.35	0.47
52	0.23	0.32
365	0.10	0.15

If the calculated value of r is greater than the tabulated value, the probability is 95% (or 99%) that there is some association between the two variables.

B.5 REFERENCES

B-1. Finney, D.J. On the Distribution of a Variate Whose Logarithm is Normally Distributed. Journal of the Royal Statistical Society, Series B, 7:155-161, 1941.

B-2. Wetherold, R.G. and L.P Provost. Emission Factors and Frequency of Leak Occurrence for Fittings in Refinery Process Units. EPA-600/2-79-044, EPA Industrial Environmental Research Laboratory, Research Triangle Park, NC. 1979.

APPENDIX C

DISCUSSION OF AMBIENT POLLUTANTS

C.1 INTRODUCTION

This section presents information on the chemicals that can be associated with a particular synthetic fuel facility and which also are of concern with respect to the possible impairment of human health and the environment. Each of the groups of chemicals should be addressed by means of the protocols for sampling and analysis presented in Appendices D-F.

Since oil shale and coal (the basic resources for synthetic fuels) arise from sedimentation of biological matter, they largely are organic substances rich in nitrogen, oxygen, and sulfur heterocyclic compounds, polycyclic aromatic compounds, and inorganic mineral impurities. Within geologic time, many of these compounds have combined to form complex organo-metallic substances. From site-to-site, oil shale and coal contain varying amounts of these materials depending on meteorological, biological, and physical forces affecting bed formation. Consequently, each particular synfuel facility can have its own chemical "signature" in terms of the ratios of these resource constituents and the types and amounts of organic and inorganic water effluents and airborne emissions. Of particular importance is that all pathways for the movement of water and airborne contaminants be monitored for compounds representative of the classes of compounds of concern.

The groupings of chemicals of concern and exemplary compounds and substances presented in this section reflect the subjective judgments of scientists participating in an ongoing program of risk analysis for adverse health and environmental effects of synfuels sponsored by the U.S. Environmental Protection Agency (C-1). Once each substance (a group of compounds, a single element or compound or a mixture) has been found to be of little or no significance, it may be dropped from further consideration. Others may be added or certain groups subdivided for further study.

The following is a brief discussion of each of the groups of the compounds of concern. Examples are provided, together with guidance to sampling and measurement protocols. For a more complete listing of the kinds of compounds emitted from synfuel facilities, the reader is referred to references C-2, C-3, and C-4.

C.2 GENERIC EMPHASIS

The following groups of compounds should be the subject of monitoring at each facility. Observed absence of certain groups over time can warrant deletion of the group (or certain constituent compounds of a group) from further monitoring.

C.2.1. Aliphatic Hydrocarbons

These are the simplest of organic compounds, containing only hydrogen and carbon. The alkanes and cyclic alkanes do not have double bonds and are relatively unreactive. The alkenes, cyclic alkenes, and dienes contain one or more double bonds and are more reactive. The alkynes have triple bonds, may be reduced to alkenes by the addition of hydrogen, or can form aldehydes or ketones upon the addition of water (C-5).

At the ambient concentrations of these hydrocarbons expected outside of the synfuel plant boundaries, no direct toxicity is expected. Volatile aliphatic hydrocarbons are not considered to be carcinogenic, mutagenic, or teratogenic, but some alkanes may be co-carcinogens or tumor-promoters (C-3). Also, they are important indicators of emissions and are precursors of other more harmful pollutants.

The following are examples of aliphatic hydrocarbons expected to be emitted from synfuel facilities:

A. Alkanes:

Methane
Ethane
Propane
Butane

Pentene
Alkanes (more than five carbon atoms)
Cycloalkanes
Polycycloalkanes

B. Alkenes:
   - Ethylene
   - Propylene
   - Butylene
   - Pentene
   - Cycloalkenes
   - Polycycloalkenes

C. Dienes:
   - Butadiene
   - Pentadiene
   - Cyclopentadiene
   - Hexadiene
   - Cyclohexadiene
   - Polycyclodienes

D. Alkynes:
   - Acetylene
   - Propyne

C.2.2 Benzene and Related Compounds

This group contains simple aromatic hydrocarbon compounds such as benzene and compounds with simple substitutions at one or more positions on the benzene ring. Benzene is a suspected carcinogen and some of the long-chain alkylated benzene derivatives are weak tumor promoters (C-6, C-1).

The following are examples of simple aromatic hydrocarbon compounds expected to be emitted from synfuel facilities:

A. Benzene and Alkylbenzenes:
   - Benzene
   - Toluene
   - Xylene
   - Propylbenzene
   - Alkylbenzene (greater than three carbon atom substitution)
   - Ethylbenzene
   - Styrene

B. Naphthalene and Alkylnaphthalenes:
   - Naphthalene
   - Methylnaphthalene
   - Ethylnaphthalene
   - Dimethylnaphthalene
   - Acenaphthalene
   - Alkylnaphthalenes (greater than two carbon atom substitution)

C. Biphenyls and Diphenyls:
   - Biphenyl
   - Diphenylmethane
   - Diphenylethane

C.2.3 Polynuclear Aromatic Hydrocarbons

Compounds in this category have two or more fused benzene rings. This group contains numerous known and suspected carcinogens (C-1). Minor changes in structure among the compounds can drastically affect respective carcinogenic properties. Thus, detailed fractionation of this group is important in analysis, as a high concentration of a weak carcinogen can "dilute" the observed effects of a potent carcinogen existent at a lower concentration in an Ames test applied to a mixture of compounds contained in this group.

The following are examples of the kinds of polynuclear aromatic hydrocarbons expected to be emitted from synfuel facilities:

Anthracenes
Phenanthrenes
Benzanthracenes
Pyrenes
Benzophenanthrenes
Chrysenes
Triphenylenes
Perylenes
Benzopyrenes
Benzochrysenes
Benzoperylenes
Fluorenes
Fluoranthenes
Benzofluoranthene
Binaphthyl
Picene

C.2.4 Heterocyclic Nitrogen Compounds

Compounds within this group contain a nitrogen atom as a member of an aromatic carbon ring. Many compounds within this group are presumed to be carcinogenic to some degree. As is the case for polynuclear aromatic hydrocarbons, minor changes in chemical structure can drastically affect oncogenic properties of these compounds (C-5).

The following are examples of the kinds of heterocyclic nitrogen compounds expected to be emitted from synfuel facilities:

Pyridines
Quinolines
Benzoquinolines
Acridines
Pyrroles
Indoles
Carbazoles
Dibenzocarbazoles

C.2.5 Heterocyclic Sulfur Compounds

Compounds within this group contain a sulfur atom as a member of an aromatic carbon ring. Since these are derived from the five-membered ring called thiophene, this group is also termed the "thiophenes" (C-5).

Many members of this group are considered to be carcinogens or co-carcinogens (C-7). Only recently has this group been rigorously studied with respect to toxicity and measurement techniques.

The following are examples of the kinds of heterocyclic sulfur compounds expected to be emitted from synfuel facilities:

Thiophenes
Benzthiophenes
Dibenzthiophenes
Naphthiophenes
Benzonaphthiophenes

C.2.6 Heterocyclic Oxygen Compounds

These compounds contain an oxygen atom as a member of aromatic or non-aromatic carbon rings. The aromatic compounds are derived from a five-membered heterocyclic ring called a furan or from xanthene which contains a six-membered heterocyclic ring (C-5).

Furan is considered highly toxic if inhaled or absorbed through the skin. Other members of this group also may be toxic, but have not been thoroughly studied (C-8).

The following are examples of the kinds of heterocyclic oxygen compounds expected to be emitted from synfuel facilities.

Furans
Benzofurans
Dibenzofurans
Naphthofurans
Xanthene
Tetrahydrofuran
Dioxane

C.2.7 Phenolic Compounds

These compounds contain one or more hydroxyl groups (-OH) attached directly to an aromatic ring. Simple phenols readily degrade under biological activity; however, complex phenols tend to be highly toxic and many have co-carcinogenic properties. They are a major component of aqueous wastes from synthetic fuel facilities. Complex phenols can be found in the particulate phase of airborne pollutants (C-1, C-9, C-10).

The following are examples of the kinds of phenolic compounds expected to be emitted from synfuel facilities:

Phenols
Cresols
Naphthol
Resourcinol
Catechol
Indanol
Phenylphenol
Hydroxyfluorene
Alkylphenols (greater than one carbon atom substitution)

C.2.8 Alcohols

Alcoholic compounds contain one or more hydroxyl groups (-OH) attached to one or more carbons of an alkyl group. These compounds can be found in aqueous airborne aerosols or in wastewaters. They can contaminate potable water and impair aquatic biota by interfering with membrane permeability.

The following are examples of the kinds of alcohols expected to be emitted from synfuel facilities:

Methanol
Ethanol
Propanol
Alcohols (with more than three carbon atoms)

C.2.9 Aldehydes, Ketones, and Quinones

These compounds contain a carbonyl group (C=O). Because of the tendency of the oxygen atom to acquire electrons, they react readily. In aldehydes the carbonyl group is attached to a simple aliphatic or aryl hydrocarbon group. Quinones are cyclic and contain two carbonyl groups (cyclic ketones contain one carbonyl group). These substances are known to be toxic; for example, certain quinones of benzo(a)pyrene may be co-carcinogens (C-1).

The following are examples of the kinds of compounds within this group expected to be emitted from synfuel facilities:

Formaldehyde
Benzoquinone
Naphthoquinone
Anthraquinone
Phenanthraquinone

C.2.10 Carboxylic Acids and Derivatives

Carboxylic acids contain one or more carboxyl groups (a hydroxyl ion attached to the carbon or a carbonyl group) attached to an alkyl or an aryl group. They readily react with bases to form salts and, by means of replacement reactions, form amides and esters as derivatives.

These diverse substances may account for 10-26 percent of the benzene-soluble organic matter associated with urban pollution. A few are known to be toxic in high concentrations; but only limited information is available regarding their biological activity at the low levels at which they normally exist in the ambient environment (C-1).

This group can be characterized using a gas chromatograph coupled with a mass spectrometer for simple acids (to C5). The identification of dicarboxylic acids, aromatic acids, aliphatic acid (greater than C5), and acids with additional functional groups may require the use of reverse phase high performance liquid chromatography (C-6).

The following are examples of the kinds of these substances expected to be emitted from synfuel facilities:

Formic Acid
Acetic Acid
Propanoic Acid
Butanoic Acid
Methylpropanoic Acid
Pentanoic Acid
Methylbutanoic Acid
Hexanoic Acid
Acetates (esters)
Phthalates (esters)
Amides

C.2.11 Amines and Nitrosamines

These compounds are generally volatile and considered a major health concern with respect to synthetic fuel facilities. Aromatic amines in particular are highly toxic. Many, together with numerous nitrosamines, are considered to be carcinogenic. They can be absorbed through the skin or inhaled.

The following are examples of the kinds of compounds within these groups that are expected to be emitted from synfuel facilities:

Primary Aromatic Amines (having more than two rings)
Aliphatic Nitrosamines
Aromatic Nitrosamines

C.2.12 Cyanide Derivatives

These substances, termed "nitriles", contain a carbon atom joined to a nitrogen atom by a triple covalent bond (C-11). They hydrolyze in water to form carboxylic acids. With heat they can decompose into toxic cyanide vapors. They also can act as catalysts in the formation of toxic nitrosamines.

The following are examples of the kinds of these substances expected to be emitted from synfuel facilities:

Thiocyanates
Nitriles

C.2.13 Trace Elements

In above-normal concentrations, many trace elements are toxic. They can accumulate in food chains, and exist primarily in combination as particles or adsorbed on other particles in air and water media.

The primary tool for the analysis of most (i.e., metals) trace elements is the atomic absorption spectrophotometer. It provides a high degree of selectivity, simplicity, sensitivity, and reproducibility for air and water samples (C-12, C-13). Other techniques used for trace element analysis include inductively-coupled, argon-plasma emission spectrometry, X-ray fluorescence, and neutron activation analysis.

The following are examples of trace elements expected to be emitted from synfuel facilities:

Aluminum
Antimony
Arsenic
Barium
Beryllium
Bromine*
Cadmium
Cerium**
Cesium
Chlorine*
Nickel
Potassium
Rubidium**
Samarium**
Scandium**
Selenium
Silicon
Silver
Sodium
Strontium**

Chromium
Cobalt
Fluorine*
Gallium**
Germanium**
Iridium
Iron
Lead
Magnesium
Manganese
Mercury
Molybdenum
Tantalum**
Terbium**
Thallium
Thorium**
Tin
Titanium
Tungsten**
Vanadium
Ytterbium**
Zinc
Zirconium**

C.2.14 Hazardous Gaseous Substances

A number of hazardous gases can be emitted from synthetic fuel facilities. These gases (e.g., hydrogen sulfide, carbonyl-sulfide, carbon disulfide, hydrogen cyanide, and gaseous vapors of metal carbonyls) can be highly toxic in concentrations possible within the workplace environment. Extremely toxic metal carbonyls persist only for five seconds, unless a high concentration of carbon monoxide exists (C-14). Highly odoriferous and persistent mercaptans are considered harmless at normal ambient levels detectable to the olfactory organs.

Examples of potentially hazardous gaseous substances expected to be emitted from synfuel facilities are:

Hydrogen Sulfide
Carbonyl Sulfide
Carbon Disulfide
Hydrogen Cyanide
Ammonia
Metal Carbonyls
Mercaptans (thiols)

C.2.15 Radioactive Materials

Due to the sedimentary origin of coal and oil shale, many radioactive elements (e.g., uranium and thorium and their decay products) have become concentrated (by a factor of ten) within the strata. Further concentration can occur during cleaning, processing, and waste concentration. Various routes can lead to both water and airborne transmission through the ambient environment. These radioactive materials can be inhaled or passed along the food chain and ingested (C-16).

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*Halogens (see Reference C-15).

**Metals requiring special spectrophotometric equipment.

Those radioactive compounds which potentially could be released into the ambient environment from synthetic fuel facilities include (C-17, C-18):

Uranium-238 and daughter products
Uranium-235 and daughter products
Thorium-232 and daughter products
Radon 220 and 222

C.2.16 Conventional Pollutants

A number of air and water pollutants are typical components of air and water monitoring programs associated with large fossil fuel facilities.

Those expected to be an integral part of a synfuels site ambient monitoring program include:

Air

- Sulfur Dioxide
- Nitrogen Dioxide
- Carbon Monoxide
- Suspended Particles
- Hydrocarbons
- Ozone

Water

- Acidity
- Chemical Oxygen Demand
- Dissolved Oxygen
- Specific Conductance (dissolved solids)
- Organic Carbon
- pH
- Temperature

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APPENDIX D

AMBIENT AIR MONITORING TECHNIQUES

D.1 CRITERIA POLLUTANTS

The principal critera pollutants are ozone, carbon monoxide, the nitrogen oxides, sulfur dioxide and total particulates. Methods for their determination are as follows:

D.1.1 Ozone

The EPA reference method for determination of ozone (O_3) is a photometric method (D-1). Ambient air and ethylene are delivered simultaneously to a mixing chamber in which the ozone reacts with the ethylene to emit light which in turn is detected by a photomultiplier at 430 nm. The resulting photocurrent is amplified and is either read directly or displayed on a recorder. The calibration procedure, which is complex, is based on the dynamic generation and standardization of ozone. This standardization involves measurement of ozone concentration using spectrophotometry (D-1). That is, absorption by ozone in a spectrophotometric cell is measured at 254 nm and O_3 concentration is calculated using Beer's Law. This method of calibration is the basis of an EPA equivalent method for ozone analysis (D-2). Another equivalent method is based on the chemiluminescent reaction which occurs between ozone and rhodamine B (D-2).

The detection limit for the photometric method is about 0.01 ppm. The typical range of the method is 0.05 to 1.0 ppm with the precision of the measurement method about 0.01 ppm at 20 percent of the upper range limit.

The analysis is typically performed using commercially available apparatus which must be EPA approved (D-3).

D.1.2 Carbon Monoxide

The EPA reference method for determination of carbon monoxide (CO) is based on the absorption of infrared (IR) radiation by CO in a non-dispersive photometer (D-4). The photometer contains two cells and two detectors. The beam of radiation from the source is split into two parallel beams. One beam passes through the reference cell and the other through the sample cell. Each detector, in this arrangement, is filled with the pure CO. When some of the latter is present in the sample beam, the sample detector receives less radiant energy by the amount absorbed by the sample component at its characteristic wavelength. The difference in signal from the two detectors is related to CO concentration. Both CO_2 and water vapor interfere in the analysis and thus standards and test samples should be matrix matched.

The detection limit of the method is about 0.05 ppm. The typical range of the method is 0.10 - 50 ppm and the precision of the method is about 0.05 ppm at 20 percent of the upper range limit.

This analysis is typically performed using commercially available apparatus which must be EPA approved (D-3).

D.1.3 Nitrogen Oxides

The EPA reference method for determination of nitrogen dioxide (NO_2) is a photometric method (D-5, D-6). The NO_2 is measured indirectly by photometrically measuring the light intensity, at wavelengths greater than 600 nm, resulting from the chemiluminescent reaction of nitric oxide (NO) with ozone (O_3). NO_2 is first quantitatively reduced to NO by means of a converter. NO, which commonly exists in ambient air together with NO_2 passes through the converter unchanged causing a resultant NO_x concentration equal to NO + NO_2. A sample of the input air is also measured without having passed through the converter. This latter NO measurement result is subtracted from the NO_x value to yield the NO_2 value. Calibration is performed with cylinders containing 50 to 100 ppm NO in N_2 with less than 1 ppm NO_2. These cylinders must be traceable to a National Bureau of Standards NO or NO_2 in nitrogen Standard Reference Material.

Interferences are limited. Unsaturated hydrocarbons react with O_3 to luminesce in the visible region of the spectrum; an optical filter is used to control this interference. Compounds such as ammonia, peroxyacetyl nitrate and some amines and organic nitrites can be converted to NO by the same system that converts NO_2 to NO and thus yield a positive interference. Other useful information regarding NO_x determination is contained in references D-7 and D-8.

The detection limit of the method is about 0.01 ppm and the typical range of the method is 0.05 to 0.5 ppm. The relative standard deviation of the measurement method is about ten (10) percent.

This analysis is typically performed using commercially available apparatus. The apparatus must be EPA approved (D-3).

D.1.4 Sulfur Dioxide

The EPA reference method for determination of sulfur dioxide (SO_2) is a wet, colorimetric method (D-9). SO_2 is collected by passing a known volume of air through a solution of potassium tetrachloromercurate. A dichlorosulfitomercurate complex is formed which is then reacted with pararosaniline and formaldehyde to form intensely colored pararosaniline methyl sulfonic acid. The absorbance of the solution is measured spectrophotometrically at 548 nm. Other useful information regarding SO_2 determination is contained in references D-7 and D-8.

The detection limit of the method in 10 ml of absorbing reagent is 0.75 μg which represents a concentration of 25 $\mu g/m^3$ SO_2 (0.01 ppm). The typical range of the method is 25 to 1000 $\mu g/m^3$ (0.01 to 0.40 ppm). The relative standard devastion of the measurement method (exclusive of sampling) is about 5 percent.

The effects of the principal known interferences, including oxides of nitrogen, ozone, and heavy metals, have been minimized or eliminated. Samples should be stored at 4°C for maximum stability.

Equivalent instrumental methods are available for SO_2 analysis (D-10, D-11). One is based on photometric detection of the chemiluminescence from sulfur atoms in a hydrogen-rich flame. This flame photometric detector (FPD) is sensitive to all sulfur-containing molecules, and gases such as H_2S must be removed prior to measurement. Species other than H_2S, such as methyl mercaptan are difficult to remove. Also the FPD signal is subject to quenching by oxygen and carbon monoxide and thus standards and test samples must be matrix matched. A typical lower detection limit for the FPD-based SO_2 analyzer is 0.005 ppm, with the range being 0.05 to 0.5 ppm and the precision at 20 percent of the upper range limit being 0.01 ppm. Any instrument used for SO_2 analysis must be EPA-approved.

D.1.5 Suspended Particulates

The EPA reference method for determination of suspended particulates in the atmosphere is based on the measurement of the particulate mass collected on a filter (D-12). In the method, air is drawn into a covered housing and through a pre-weighed glass fiber filter by means of a high-flowrate blower at a rate of 40 to 60 ft^3/min. The system design in combination with the flow rate results in particles within the size range of 100 to 0.1 μm diameter being collected on the glass fiber filter. The mass concentration of suspended particulates in the ambient air (μg/m^3) is computed by measuring the mass of collected particulates and the volume of air sampled.

Concentrations as low as 1 μg/m^3 can be measured by sampling at 60 ft^3/min for a period of 24 hours. The reproducibility of the method is about 4 percent. The error in the measured concentration may, however, be in excess of ±50 percent. This inaccuracy is due in large part to changes occurring in the airflow rate which, in turn, is affected by the concentration and nature of the particulate material being collected.

Equipment needed for sampling includes the sampler, a sampler shelter, a rotameter, an orifice calibration unit, a differential manometer, a barometer, and a positive displacement meter. Analysis requires a chamber for conditioning the filters, an analytical balance capable of weighing 8 by 10 in. filters to 0.1 mg, and a light source for checking for holes in the filters. Glass fiber filters should have a collection efficiency of at least 99 percent for particles 0.3 μm diameter. All this equipment may be purchased.

D.2 HAZARDOUS GASES

The principal hazardous gases of concern are ammonia, hydrogen, cyanide, hydrogen fluoride, total hydrocarbons, and sulfur gases (H_2S, COS, CS_2). Methods for their determination are as follows:

D.2.1 Ammonia

Ammonia is collected by passing a known volume of air through a diluted solution of sulfuric acid in an impinger. Several different methods are available for measurement of the ammonium sulfate produced during sampling. In one method, the ammonium sulfate is mixed with Nessler reagent to produce a yellow-brown complex. Ammonia concentration is then determined by measuring the absorbance of the solution at 440 nm (D-13, D-14). The range of the method is 20 - 135 ppm. The only interferent reported is that of ammonium salts, which can be removed by filtration of the air before entry into the impinger The method does not distinguish between free and combined ammonia. A more sensitive method involves reaction of the ammonium sulfate with phenol and alkaline sodium hypochlorite to produce indophenol, a blue dye which is measured colorimetrically (D-7). Analyses in the 1 to 30 ppb range with a relative standard deviation of 30 percent are possible with this method, though it is prone to interferences. Certain metal ions and particulate material must be removed from the air before being passed through the impinger. The only instrument required is a spectrophotometer operating in the visible range. Finally ammonia can be determined using the ammonia-selective electrode (D-15); metals which complex ammonia will interfere with this method and the method of standard additions should be used as a quality control measure.

D.2.2 Cyanide Compounds

Cyanide is collected by passing a known volume of air through an impinger containing 0.1 N sodium hydroxide (D-16, D-17). The cyanide collected is measured using a cyanide ion specific electrode. This ion specific electrode in conjunction with a reference electrode gives rise to a potential which is related to the logarithm of the cyanide concentration. The range for the method is 0.013 to 13 mg/m^3 in air. The only significant interferent is sulfide, which must be removed through precipitation as cadmium sulfide if present. The equipment needed for this determination includes a cyanide ion specific electrode, a reference electrode and an expandable scale, mV/pH meter.

Colorimetric and titrametric procedures for measurement of the collected cyanide are also available (D-18) and should be performed to verify the applicability of the electrode method when the latter is preferred.

D.2.3 Fluorides

Fluorides are collected by passing a known volume of air through impingers containing 0.1 N sodium hydroxide (D-19, D-20). The fluoride collected is measured using a fluoride ion specific electrode. This ion specific electrode, in conjunction with a reference electrode, gives rise to a voltage signal which is related to the logarithm of the fluoride concentration. A special buffer prepared with glacial acetic, sodium hydroxide, sodium chloride and cyclohexane diamine tetraacetic acid monohydrate (CDTA) must be added to the collected sample prior to measurement to prevent interference by hydroxide ion and ions of silicon, iron and aluminum. The range for the method with a 40-liter sample is 0.05 to 475 mg/m^3 of air and the relative standard deviation for sampling and analysis of 100 µg HF is about 7 percent.

The equipment needed for this determination includes a fluoride ion specific electrode, a reference electrode and an expandable scale mV/pH meter.

D.2.4 Total Hydrocarbons

Total and non-methane hydrocarbons in ambient air are measured using a flame ionization detector (FID) (D-21, D-22). This device consists of a hydrogen/air burner and two electrodes; hydrocarbons entering and decomposing in the flame give rise to ions which conduct current between the electrodes. This current is measured and is proportional to the number or concentration of carbon atoms in the flame. Thus one molecule of butane would give twice the signal of one molecule of ethane. Methane concentration, which is usually significant, is not of particular interest as it is considered photochemically unreactive. Various schemes are used to separate methane from the rest of the hydrocarbons. Some of the commercially available instruments use gas chromatographic columns to separate the methane from the other hydrocarbons. The total organic concentration (TOC) and the methane are measured separately and the non-methane organic concentration is calculated by difference. In other systems TOC is measured and then all organic compounds except methane are catalytically oxidized and the methane is measured alone. Again NMOC is calculated by difference. In still other systems the oxidized compounds are reduced to methane and measured as NMOC directly using the FID. NMOC can be measured directly using FID after collection in a cryogenic trap which does not collect methane. The TOC measurement is depressed by moisture, often producing negative NMOC values.

Also inaccuracies are inherent with the subtraction of large numbers (methane) from slightly larger numbers (TOC)(D-23). The minimum detection limit for the method is about 0.05 ppm as carbon The typical range for the method is 0.5 to 10 ppm C and the precision is about 0.10 ppm C for TOC.

D.2.5 Hydrogen Sulfide, Carbon Disulfide and Carbonyl Sulfide

A variety of methods are available for analysis of the individual sulfur compounds (D-8, D-24). It is most cost effective however to use a single method for determination of all three compounds (D-25, D-26). This method is based on measurement using a gas chromatograph fitted with a flame photometric detector. In the method an aliquot of air is loaded onto a column suitable for separation of the sulfur gases. The separated gases are then measured. Compounds eluting after the sulfur compounds are usually vented without passing through the FPD.

The lower detection limit for the FPD-based analyzer is about 0.005 ppm. The relative standard deviation is typically about ten (10) percent.

D.3 ORGANIC COMPOUNDS

D.3.1 Sampling Vapor Phase Organic Compounds

Sampling methods for vapor phase organics generally involve the passage of a measured amount of air through a device containing a solid sorbent. Organics are removed by adsorption to the solid, and are thus transported to laboratory facilities for later analysis. Prior to the adsorption process, the air is usually filtered to remove particulate matter. The chief benefit of this approach is that it allows for significant concentration of the sample component prior to analysis. Since ambient air levels are almost always low for most organics (≤ppb levels), some form of concentration is needed. Other collection methods such as cryogenic collection and the use of impingers also provide component concentration. Whole air sampling, which simply consists of a grab sample (evacuated cannister, bay, etc.) and direct analysis of a portion of the sample is less often applicable due to the lack of component concentration.

Because of the low concentrations of ambient air organics, collection techniques are exacting, and require experienced personnel for proper method application. Rigorous attention must be paid to logistical detail for sample collection schedules, sample storage and transport. Some detail on various ambient air sampling methodologies can be found in an American Public Health Association publication (D-27). Specific methods, applicable to synfuels facilities, are summarized below.

D.3.1.1 Sorbent Trapping--

The most commonly used materials for collection of ambient air samples are polymeric sorbents and carbon sorbents. Inorganic materials such as silica gel or alumina have been used, but surface deactivation by adsorption of water from the air has limited their application to the collection of certain polar compounds.

The polymeric materials most commonly used are Tenax GC® and Amberlite resins such as XAD-2. For some specific compounds (e.g., halogenated aromatics), polyurethane foam (PUF) has also been used. Tenax has a very low affinity for water, and is thermally stable (up to ca. 300°C), hence collected organics may be removed for analysis by thermal desorption. XAD-2 and PUF lack thermal stability, and are solvent rinsed for compound desorption. Tenax is useful for collection of compounds boiling between ca. 60° and 300°C, while XAD-2 and PUF are useful for compounds with boiling points above ca. 150°C.

Carbon adsorbents have relatively low affinity for water, and strong affinity for unsaturated organic molecules, particularly aromatics. This allows for the collection of certain low boilers that are not efficiently trapped by polymeric sorbents. Carbon adsorbents consist of activated charcoals, carbon molecular sieves and carbonaceous polymeric sorbents.

D.3.1.1.1 Procedure--The chosen sorbent is prepared for sample collection using rigorous and well defined procedures. In the case of Tenax GC, the polymer is solvent extracted, dried, sieved to a specified mesh size range, packed into sampling cartridges, and thermally desorbed under ultraclean helium purge (D-28, D-29). The high affinity of Tenax for organics requires extremely tight control over the entire preparation process. Other resins are similarly prepared, with omission of the thermal desorption step if the resin (e.g., XAD-2 or PUF), is unstable at higher temperatures.

After being suitably sealed (double containers) for transport to the field, the sampling cartridges are fitted with a filter (glass fiber, Teflon, etc.) on the upstream end, and attached to a sampling pump. Sampling rates depend on the sorbent used, the compounds monitored, and a number of other factors. All pertinent sampling information is recorded (pump flow rate, start/stop times, weather information, sampling location) in log books. After collection is complete, the sampling cartridges are resealed in appropriate containers for transport to the analysis laboratory.

D.3.1.1.2 Effort--Substantial effort is required for pre-field activities involving sorbent cartridge preparation, particularly for Tenax GC. Since ambient monitoring involves collection and analysis of relatively low levels of organics, sorbents must be rendered, and maintained, contaminant free. For sorbents with a high affinity for organics (e.g., Tenax GC), the preparation cycle (solvent washing, drying, sieving, packing, desorption) can take up to 1 week for a batch of Tenax GC sufficient for ca. 120 cartridges. Approximately 24 person-hours are required for this procedure.

For resins such as XAD-2 or PUF, with no thermal desorption step, ca. 16 person-hours are required for preparation of up to 1 kg of XAD-2.

Carbon sorbents generally require only packing in sampling tubes followed by thermal desorption. Total effort required is ca. 8 person-hours for the preparation of up to 50 cartridges.

D.3.1.2 Impinger Collection--

Collection of ambient organics from air via the use of impingers (bubblers) involves the passage of a measured volume of air through a liquid in which the target organics are trapped. The impinger usually consists of a tubular glass reservoir with a gas inlet tube fitted so that the incoming gas stream is introduced into the liquid near the bottom of the reservoir. To increase the contact between the air stream and the liquid trapping medium, the air is dispersed by the use of fitted diffusers or capillary jets. Generally a number of impingers are connected in series to ensure quantitative collection of analytes. To prevent evaporation of reservoir liquid during collection, the impingers can be cooled (e.g., ice water bath). The reader is referred to Stern (D-8) for details on impinger design.

Impingers are commonly used to collect organics in solutions containing derivatizing reagents. The formation of derivatives of target compounds is usually carried out to enhance the detectability of certain species.

Aldehydes for example can be collected in solutions of dinitrophenylhydrazine which convert them to stable non-volatile highly chromophoric hydrazones. Analysis can be conducted later using chromatographic/spectroscopic techniques (D-30, D-31).

D.3.1.3 Cryogenic Collection--

Ambient air organics can be collected by the passage of a measured air sample through a cold trap. Depending on the refrigerant used, various components will be condensed and thus collected for subsequent analysis. The method has the advantage of providing a concentrated sample of air vapors in a form that is immediately available for analysis. Stern (D-8) provides details of the methodology; Rasmussen (D-32) has reported on a portable cryocondensing sampler.

Commonly used refrigerants include liquid nitrogen or argon, and dry-ice/solvent mixtures. The trap, usually consisting of a metal tube (stainless steel, nickel), is arranged such that the trap contents can be valved directly to the analytical device (e.g., GC). Sample transfer is accomplished by flash heating with gas purge. The method requires that the entire sampling/analysis system be used in the field, or that a whole air sample is collected for transport to the cryogenic collection device. An important factor in the consideration of the use of this approach is the concentration of relatively large amounts of water, which can block the trap (as ice), and serves to create a potentially high acid solution by dissolution of NO_x and/or SO_2.

D.3.1.4 Whole Air Collection--

Whole air samples can be collected for transport to the analytical laboratory for subsequent analysis. Evacuated containers are most commonly used for sample collection, although samples can be taken by pumping air through a bulb or other device, and sealing inlet and outlet after passage of a suitable volume of air. Specific collection methods are dealt with in some detail by a National Academy of Sciences monograph (D-33).

Rigid containers (glass, metal bulbs, gas-tight syringes) are advantageous in that sample loss due to permeation and/or leakage is generally minimal. However, losses of certain species through adsorption or reaction with container surfaces may be a problem. The use of non-rigid containers (e.g., Teflon, Tedlar bags) minimize adsorption problems, but limit the time between sampling and analysis due to permeation of collected materials out of the bag and contaminants into the bag.

Whole air collection is not readily useful for ambient air monitoring unless some form of sample concentration (e.g., cryofocussing) is employed prior to analysis.

D.3.2 Sampling Semi- and Non-Volatile Airborne Organic Compounds

Non-vapor phase organics are present in ambient air in a particle-bound state by virtue of adsorption to airborne particles. Semi- and non-volatile compounds include, generally, those with boiling points greater than 150°C. Many types of sampling devices are available for the collection of air aerosol. These devices utilize principles of filtration, centrifugation, impaction or electrostatic precipitation. Filtration is by far the most important for organics collection, due to the relatively large amount of particulate trapped. Cyclones and impactors* are most commonly used for particulate characterization (size, weight, inorganic content, etc.), and generally collect too little material for analysis of adsorbed organics (such organics usually comprise ca. 1-10% by weight of ambient air aerosol). Thus for monitoring for semi- and non-volatile organics at synfuels facilities, only filtration will be addressed as the most practical collection procedure.

D.3.2.1 Filtration--

A typical level of ambient air particulate is ca. 50 $\mu g/m^3$. In order to obtain a sufficient quantity of particulate for organic analysis (ca. 50 mg) some 1000 m^3 of air would need to be sampled. To collect the requisite amount of particulate in less than 24 h, sampling rates of ca. 1 m^3/min are required. These rates are available through the use of the Hi-Vol sampler, a commercially available device that has been used extensively for many years. Warner (D-35) provides a thorough description of the sampler.

The filter media used with the Hi-Vol sampler consist of glass or quartz fiber mats. Glass fiber filters can be obtained that are Teflon® coated to reduce surface activity. Cellulose and membrane filters are not amenable to high volume air sampling, and thus would have limited application to synfuels organics monitoring programs. Mitchell (D-36) provides a complete discussion of filter media.

Collected particulate mass (from the Hi-Vol) is determined by weighing tared filters under controlled humidity conditions. The entire filter, with particulate, is then extracted for organics analysis.

D.3.3 Analytical Techniques for Determination of Organic Compounds

A relatively small number of basic analytical techniques are currently successfully used for ambient level monitoring of air, water and soil. Most involve well-developed chromatographic methods, and utilization of a variety of detection systems to achieve requisite sensitivity and selectivity.

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*The Massive Air Volume Sampler (D-34) utilizes principles of impaction and electrostatic precipitation, and is capable of collecting very large quantities of particulate. This capability and the sampler's expense render the device not useful for routine monitoring for synfuels facilities.

Spectroscopic techniques are used either in conjunction with chromatography systems, or as stand-alone devices for specific analyses.

A brief, general description of those techniques most commonly employed in ambient level monitoring programs is provided prior to a discussion of specific methodologies. These descriptions were taken, in part, from a draft EPA report ("Technical Assistance Document for Sampling and Analysis of Organic Compounds in Air", by R. W. Rigging, Battelle Columbus Laboratories, November, 1982).

Gas chromatography (GC) is by far the most widely used technique for environmental monitoring. It is applicable to all compounds that possess sufficient thermal stability and volatility, and can utilize a wide variety of detection modes.

GC basically is a separation technique wherein components of a sample are separated by differential distribution between a gaseous mobile phase (usually helium, nitrogen, or hydrogen carrier gas) and a solid or liquid stationary phase held in a glass or metal column. Sample is injected into the carrier gas as a sharp plug and individual components are detected as they elute from the column at characteristic "retention times" after injection. Many basic texts are available for a detailed description of GC principles and applications; Katz (D-27) represents one of many examples.

Analysis by GC is conducted using either packed columns or capillary columns. The former consists of a relatively wide bore (typically 2-6 mm) column filled with an inert support material coated with a liquid film of stationary phase. Capillary columns have very small bores (<500 μ), with the walls of the tubing coated with liquid stationary phase. For a number of reasons, capillary columns are superior to packed columns in terms of resolution, and have found wide application for environmental analysis. A complete discussion of capillary column technology is provided by Jennings (D-37) and Bertsch _et al_. (D-38). A wide variety of GC detectors are useful for pollutant monitoring. The flame ionization detector (FID) is the most popular detector, and the one with the most universal response. Virtually any carbon-containing molecule can be detected with the FID. The electron capture detector (ECD) is useful for detection of electron deficient molecules and can provide high selectivity and sensitivity for such molecules. The photoionization detector (PID) is selective for photoionizable molecules and is especially suitable for the highly sensitive detection of aromatic compounds. The Hall electrolytic conductivity detector (HECD) can be operated specifically for detection of halogen, sulfur, or nitrogen-containing species. Other less commonly used detectors include the flame photometric detector (FPD), which is useful for sulfur or phosphorus-containing compounds, and the alkali flame (AFD), and thermoionic specific (TSD) or nitrogen-phosphorus (NPD) detectors; these detectors are selective for nitrogen or phosphorus and are more sensitive than either FPD or FID. Specific GC application usually determines the mode of detection.

Another general analytical technique that has found widespread application for environmental analysis is gas chromatography/mass spectrometry (GC/MS). In simple terms the technique can be viewed as gas chromatography with a mass spectrometer as a detector. The benefits of this approach include high analytical sensitivity and specificity, the latter sometimes minimizing the sample purification effort required. In the mass spectrometer, the sample components are ionized and fragmented into characteristic spectral patterns by continuously scanning GC effluent as it is introduced into the mass spectrometer. Complete mass spectral scans (40-600 amu) can be produced as often as 1/second. It is also possible to operate the spectrometer in a selected ion monitoring mode or multiple ion detection mode wherein only a few selected ions are monitored rather than scanning a broad mass region. These approaches provide increased sensitivity for monitoring for specific compounds. The data output from a GC/MS system can be prodigious, and various mass storage devices (usually magnetic tape) and sophisticated software are employed for data archiving and reduction. Several textbooks are available for more comprehensive discussions of the technique of GC/MS (e.g., D-39); environmental applications using GC/MS have been addressed by Burlingame (D-40).

For those compounds not amenable to gas chromatographic separation, either by virtue of being nonvolatile or thermally labile, the technique of high performance liquid chromatography (HPLC) is used. This methodology employs closed chromatographic columns consisting of small diameter particles, either uncoated or coated with liquid phase, over which mobile phase can be passed. Because of the size of the column packing particles high pressures are required to obtain optimum solvent flow for which various types of sophisticated solvent delivery systems are utilized. Currently available instrumentation allows for the selection of a wide variety of flow rates and adjustable mobile phase compositions. Several authors (e.g., Parris, D-41) have written detailed texts describing methodology, instrumentation and application. HPLC is most commonly utilized in ambient air monitoring programs for semi-volatile compounds such as polycyclic aromatic hydrocarbons and for compounds such as aldehydes which are usually determined as nonvolatile derivatives. Most HPLC systems utilize UV absorbance and/or fluorescence emission detection systems. Recent advances have shown the feasibility of interfacing a mass spectrometer to an HPLC thus bringing the same advantages to this technique as are currently enjoyed by gas chromatography (D-42, D-43).

Other chromatographic techniques such as column chromatography and thin-layer chromatography are used primarily for sample purification or "clean-up" prior to determination by more sophisticated separations methods. Stern (D-44) discusses thin-layer chromatography.

D.3.4 Measurement of Organic Vapors

With generally few exceptions, ambient levels of organic vapors are low, and the procedures and techniques required for analysis must therefore embody high performance capability. This entails the use of research grade equipment, some of it very sophisticated and expensive, and highly skilled chemists well trained in trace analysis.

This section addresses the general analytical approaches most effectively utilized for the determination of organic vapors following collection.

D.3.4.1 Solid Sorbent/Thermal Desorption Analysis--

For those compounds collected on certain heat-stable sorbents (e.g., Tenax GC®, charcoal, Chromsorb®), analysis is conducted by gas chromatography (GC) or gas chromatography/mass spectrometry (GC/MS). The selectivity of GC/MS renders that technique more useful for the complex mixtures likely to be found in air samples. For the same reasons high resolution capillary columns are usually a necessary component of the GC system, although in certain cases, for example the monitoring of single, selected compounds, packed columns can provide sufficient resolution for analysis (D-33).

D.3.4.1.1 Procedure--Sorbent cartridges containing the collected vapor phase components are analyzed either directly, or, for quantitative analysis, after loading with measured quantities of reference standards. Such loading, for reference standards or for the preparation of control cartridges, is accomplished most expeditiously via a permeation system (D-45).

The sample cartridge is placed in a unit suitable for heat desorption with a purge gas and collection of the desorbed components in a cryogenic trap. A commercial version of such a device has been described (D-46). Following desorption and collection of the condensed vapor-phase components, the cryotrap is rapidly heated and purged, thereby transferring the sample to the GC column as a discrete low-volume injection. Analysis thus proceeds using either GC with a variety of detectors (*e.g.*, flame ionization, electron capture, flame photometric, photoionization, etc.), or GC/MS using a variety of operational modes (*e.g.*, selected ion monitoring, multiple ion detection, full scan, etc.). The use of GC/MS in environmental research has been reviewed (*e.g.*, D-47). A typical example of the use of solid sorbent/thermal desorption analysis for organic vapors in ambient air is provided by Pellizzari *et al*. (D-45, D-48).

D.3.4.1.2 Performance Parameters--Detection limits for most vapor phase compounds, when analyzed by GC using flame ionization detection, range from *ca*. 1-100 ppb; the volume of air sampled directly affects this figure. For certain classes of compounds (*e.g.*, amines, halogenated species), specific detectors (*e.g.*, nitrogen-phosphorous detector, electron capture detector) can provide lower limits of detection and enhanced selectivity. Detection limits for thermal desorption analysis using GC/MS range from *ca*. 100 ppt-100 ppb depending on compound, volume of air sampled and MS operating mode. Precision and accuracy for both GC and GC/MS methods are limited by sample collection procedures, sample storage time, performance of the desorption unit and GC or GC/MS, and on the physical/chemical properties of the target compounds. Accuracies of ±10-40% have been reported for GC/MS analyses (D-45).

Interferences can be a problem in the analyses of some compounds with certain sample collection procedures. Proper use of blanks and controls is essential to minimize the magnitude of the problem. For sorbent trapped material, sampling in caustic or high level halogen-containing atmospheres should be conducted with caution.

D.3.4.2 Solid Sorbent/Solvent Desorption--

Higher boiling (i.e., > ca. 150°C) vapor-phase air pollutants are usually collected via sorbents such as Amberlite® XAD-2 (styrene-divinylbenzene copolymer), or polyurethane foam (PUF). These materials are not thermally stable, and the trapped sample components are removed by solvent rinsing. Amberlite XAD-2 resin is specified as the vapor-phase trap component of the EPA promulgated stationary source sampler (SASS train). A description of the analytical methods used for the XAD-2 trapped materials is provided in an EPA report (D-49). A detailed description of the solvent desorption procedures and analytical methods for PUF samplers is provided by Lewis et al. (D-50).

D.3.4.2.1 Procedure--The removal of relatively nonvolatile vapor-phase substances from polymeric sorbents is accomplished via the use of Soxhlet (or Soxhlet-type) extraction. The sorbent is placed in the receiver of a Soxhlet apparatus, and extracted for a prolonged period (ca. 4-24 h) with an appropriate solvent. Following extraction the sample solution (usually ca. 100-1000 mL) is concentrated using solvent removal techniques that minimize evaporative or adsorptive sample loss. Careful rotary evaporation, Kuderna-Danish techniques and/or nitrogen blow-down are commonly used procedures. The concentrated sample (ca. 0.1-10 mL) may be analyzed directly, or may require chromatographic purification. In the latter case alumina or silica gel column chromatography has been used to obtain fractions containing the analyte(s) in a form amenable to direct analysis (D-28, D-29).

Gas chromatography has been used most often for the analysis of the solvent desorbed compounds, although any of a variety of instruments (e.g., HPLC, AA, etc.) may be used. Any chromatographic procedure will utilize direct liquid injection for sample introduction; this means that only approximately 1-10% of the sample is available for direct analysis. Replicate analysis can be conducted, a feature not possible with thermal desorption processes. As noted earlier, the use of capillary vs. packed columns, and certain specific detectors can enhance analytical performance. The choice of column and detector are dictated by the specific site-monitoring requirements, and by the analytes monitored.

D.3.4.2.2 Performance Parameters--Overall method sensitivity for solvent desorption of sorbed compounds is generally less than for thermal desorption. This is primarily due to the inability to analyze for more than a fraction of the sample at a time (vide supra). In addition there is more sample handling (extraction, concentration, purification) associated with the solvent desorption procedure, and hence greater potential for sample loss. These factors are somewhat offset by the ability to sample larger volumes of air using XAD-2® or PUF, than, say, Tenax GC®.

Precision and accuracy are highly dependent on the specific analytical procedure adopted; both suffer because of the greater degree of sample manipulation inherent to this method, particularly if chromatographic clean-up is required. The working range of compound quantitation is defined by the analytical instrumentation, since the sample concentration can be adjusted to ensure compatibility.

D.3.4.3 Cryocollection Analysis--

The analysis of cryocollected samples depends to some extent on the particular method of sample collection. For some cryosamplers (D-32), selective distillation and recovery of fractions is possible. Most samplers provide for syringe removal of gas samples for analysis. Some constraint is imposed on the sampling and analysis system since cryogenic temperatures must be maintained on the sample between time of collection and time of analysis.

D.3.4.3.1 Procedure--Cryocollected samples are analyzed by GC. Virtually any detector, including MS, can be used. Sample aliquots are withdrawn from the cryocondensor vessel with a gas-tight syringe and injected into the GC. Alternatively, the cryotrapping system can be interfaced directly to the GC via a multi-port valve (D-51). This approach requires that the sampling and analysis system be transported to the monitoring site.

D.3.4.3.2 Performance Parameters--The overall system performance for the analysis of cryogenically collected samples is dependent on the volume of air collected, and on the specific performance characteristics of the GC or GC/MS. The concentration of air contaminants during collection usually allows for the analysis of compounds in the ppb range. The use of selective detectors such as electron capture or photoionization can significantly enhance detectability over the flame ionization detector.

Rasmussen (D-32) has reported extremely good precision (*ca*. 1-3%) for the repeated collection of air samples under laboratory conditions. The efficiency of collection is normally very high particularly for those samplers that employ low temperature coolants (liquid nitrogen, oxygen, etc.).

D.3.4.4 Impinger Collection Analysis--

Samples collected by impingement in a liquid are concentrated to some degree, depending on the efficiency of collection and volume of trapping medium. Further concentration of the liquid solution is possible if the sample components (or derivatives thereof) are nonvolatile. By far the most common use of impingers is for collection and simultaneous derivatization of certain air pollutants. The prime benefit to the analyst of converting samples to derivatives is the enhanced detectability of the sample. For example carbonyl compounds such as formaldehyde and acetone, which have no significant UV absorption, are quantitatively converted to 2,4-dinitrophenylhydrazone (DNP) in impingers. The hydrazones possess generally intense chromophoric properties, and thus render the carbonyl components at once nonvolatile and readily amenable to HPLC analysis using UV absorption detection. Other derivatization procedures are possible for compounds such as phenols, amines and phosgene. The procedure presented below describes the analysis of impinger-collected aldehydes (as DNP), and is representative of such methods generally (D-30).

D.3.4.4.1 *Procedure*--Impinger solutions of acidic 2,4-dinitrophenylhydrazine are used to convert airborne aldehydes to the stable, nonvolatile, UV-absorbing hydrazone. Five to thirty liters of air are bubbled through two serial impingers at 0.5-1.5 L/min. The impinger solutions are combined and extracted with chloroform. The extracts, after washing with acid and distilled water, are concentrated to dryness under mild vacuum. The residue is then dissolved in 2 mL of acetonitrile and analyzed by HPLC. Isocratic mobile phase compositions of *ca*. 70:30 acetonitrile:water are employed with a reverse phase column. Column eluant is monitored by UV detection (254 nm); quantitation is accomplished by comparison of detector response to calibration curve values.

D.3.4.4.2 Performance Parameters--The method is applicable to virtually all simple aldehydes and ketones, from formaldehyde to tolualdehyde and acetone to methyl-*n*-amylketone. Detection limits were reported as 0.1 ng for formaldehyde; 0.2 ng for C-2 and C-3 aldehydes; and 0.5 ng for higher alkane and aromatic aldehydes. These values correspond to air levels of *ca*. 1.5-2.6 ppb. Recoveries of test compounds prepared by spiking impinger solutions ranged from 81-103%. Analytical precision for recovery studies ranged from *ca*. 2-8% relative standard deviation. Determinations of levels of vapor phase aldehydes prepared as a test mixture showed precision for 5 replicates, of *ca*. 1-7% RSD. The method has been used for the determination of vapor phase aldehydes in urban air, industrial emissions, automobile exhaust and tobacco smoke.

D.3.5 Measurement of Aerosol Organics

The analysis of air aerosol for adsorbed semi- and non-volatile organics has been conducted, at least for certain compounds, for many years. Although a number of different specific procedures have been developed and utilized, most are similar in one respect or another. General analytical approaches for aerosol organics are available from a number of sources such as Stern (D-44) and the National Academy of Sciences (D-52).

The basic analytical methodology involves extraction of collected particulate with organic solvent, purification of the extracted material, and analysis by any of several methods depending on target materials. A vast body of literature is available for the analysis of polycyclic aromatic compounds (PAC), and the methods used for these compounds are generally representative of procedures for aerosol organics. Methods for PAC analysis are deemed most pertinent for synfuel processes monitoring. The methods are usually based on particulate collection using Hi-Vol samplers, although particulate collected by any means can be incorporated into the methods described below.

D.3.5.1 Procedure [Method 1, polycyclic aromatic hydrocarbons (D-53)]--

Filter material (glass fiber, Teflon, etc.) containing collected particulate is placed in cyclohexane and sonicated for 1 h. The solution is filtered (0.5 μ Teflon), and the filtrate passed through a silica gel cartridge

(Waters Assoc. Sep-Pak, or equivalent). The silica cartridge is washed with ca. 5 mL of hexane:methylene chloride (9:1). The wash solution is concentrated to ca. 2 mL, mixed with ca. 1 mL acetonitrile, and concentrated to ca. 0.1 mL. The concentrated extract is then streaked onto a cellulose TLC plate. After developing the plate in the specified solvent system, the band corresponding to the PACs is scraped, and the collected cellulose is sonicated with acetonitrile. This solution is centrifuged, and an aliquot of supernatant is injected onto a reverse phase HPLC column. The eluant is monitored using a fluorescence detector (340 ex; >425 em). Quantitation of selected target PACs is accomplished by comparison of detector response with calibration curve values.

D.3.5.1.1 Performance Parameters--The lower limit of detection for most PACs corresponds to ca. 100 ng/m^3. Precision and accuracy are not specified in the NIOSH protocol. The TLC clean-up step can be problematic, giving non-reproducible elution times. The number and similarity of many PACs prevent complete resolution by HPLC; confirmatory techniques for certain target compounds may need to be employed.

D.3.5.2 Procedure [Method 2, polycyclic aromatic compounds (D-54)]--

Filter media (glass fiber, Teflon-coated glass fiber) containing collected particulate is Soxhlet extracted with methylene chloride, and the extract is concentrated via rotary evaporation and nitrogen blow-down. The extract is subjected to an aqueous acid/base wash sequence to separate bases, acids and neutrals. The neutral fraction is then separated into 4 fractions by open column silica gel chromatography. The polycyclic aromatic hydrocarbons elute in a single fraction, and are free of less polar materials (alkanes), as well as more polar compounds (oxygenated species, heterocyclis, etc.). The fraction is concentrated and analyzed by fused silica capillary column GC/MS. Compounds are identified by their mass spectra and retention time; quantitation is achieved by reference to a sample standard using pre-calculated response factors. For certain compounds negative ion chemical ionization can be used to achieve lower limits of detection and quantitation.

D.3.5.2.1 Performance Parameters--The method is applicable to particulate samples containing up to 1 g of organic extractables. Overall method sensitivity depends on sample size; ambient levels of most PACs are easily within reach of the method. Recoveries of organics through the procedure range from 75-104%.

D.4 INORGANIC SPECIES

The inorganic species of concern in air are metals and anions. These usually will be associated with particulate material. A few metals such as selenium and mercury can be found in the vapor state in air. Background information on the toxicity of trace elements and their presence in emission from synthetic fuel plants is contained in references (D-55 - D-60).

The high volume sampler described under CRITERIA POLLUTANTS can be used to collect samples for analysis. Samples also can be collected with smaller systems using smaller filters, e.g., 47 mm (D-7, D-8, D-12, D-58). Metals in their vapor state such as mercury and selenium are collected by drawing a known volume of air through an oxidizing medium such as potassium permanganate or potassium persulfate solution in an impinger (D-61).

D.4.1 Metals

The metals collected on filters can be analyzed in several different ways. The filters can be analyzed directly, without treatment, using x-ray fluorescence (XRF) (D-62, D-63). The filters are placed in the x-ray system in a multifilter cassette and are automatically analyzed. About 30 elements can be measured simultaneously this way ranging from aluminum (atomic number = 13) to barium (atomic number = 56). Minimum detectable limits range from 20 ngm/cm^2 of filter for aluminum to 3 ngm/cm^2 of filter for selenium. The x-ray apparatus for air filter analysis may be purchased and used in-house. Commercial laboratories also are available to perform x-ray analysis.

The filters can also be analyzed directly using neutron activation analysis (NAA) (D-64). This technique can be used to measure most of the elements of concern, but when many different elements are present together on a filter, interferences occur and detection limits are high, usually in the range of micrograms per filter. However, with sufficient sample material, elemental levels in air at the ngm/m^3 level can be measured. Neutron activation analysis instrumentation is expensive and this type of analysis is best performed by a commercial laboratory.

The metals also may be measured using spark source mass spectrometry, atomic absorption spectrophotometry or inductively-coupled, argon plasma emission spectrometry. All three techniques require that the metals be dissolved from the filter; this is best done by extraction with dilute acid. Organometallic compounds present must be decomposed using the Parr bomb combustion technique. Combustion must also be performed if the organic level in the particulate material is high, as it will interfere in the measurement process, especially for spark source mass spectrometry.

Spark source mass spectrometry (SSMS) is a very useful technique as it permits simultaneous measurement of essentially all the elements (D-65 - D-67). Assuming 50 mgm of particulate are collected, minimum detection limits range from about 0.05 $\mu g/m^3$ for manganese to about 5 $\mu g/m^3$ for cadmium. The method is fairly imprecise, usually about ± 30 percent. This poor precision and the fact that the technique can be used to measure essentially all the elements make this a good screening technique. Finally the equipment is very expensive and analyses are best performed by an outside, commercial laboratory.

Atomic absorption spectrophotometry (AAS) with electrothermal atomization provides the lowest detection limits of the various methods available (D-68, D-69). These detection limits range from 0.5 to 100 ngm/mL of metal extract solution. As many as 67 elements can be measured by atomic absorption spectrometry and the precision of the technique is about ± 2 percent for most elements at mid-range (D-70). The linear response range usually spans two orders of magnitude. The principal limitation of the technique is that only one element at a time can be measured. However, the newest computer-controlled atomic absorption spectrometers can be programmed to change light sources, wavelength settings, etc., so that about ten (10) elements can be determined in each of 30 to 50 samples without operator attention.

The final method to be discussed is inductively coupled, argon-plasma atomic emission spectrometry (ICP-ES) (D-71, D-72). One form of this instrument permits the simultaneous measurement of up to 50 elements; the other and much less expensive form measures the elements sequentially under computer control. The minimum detection limits for ICP-ES are about ten (10) times those of AAS. An advantage of the technique is its wide linear response range, which for many elements extends over five (5) orders of magnitude with a precision of several percent. ICP-ES is not as selective as AAS, with emission lines from certain elements in the sample overlapping emission lines of other elements. The sequential analysis instrument does allow one to select alternate emission lines if the primary lines have interferences.

D.4.2 Ions

The extractable ionic species chloride, nitrite, nitrate, sulfate, phosphate and ammonium are best measured using ion chromatography (D-73, D-74). This method involves injection of the aqueous filter extract onto an ion exchange column. Eluent is forced through the column resulting in separation of the ions. The effluent of the first column passes into a second column which neutralizes the elution medium. The ions emerge from the second column in this neutral medium which then is passed through a conductivity cell. The ions passing through this cell give rise to a measurable signal. One type of column and eluent is used for determination of anions and another for determination of cations. The ion chromatograph is commercially available. The minimum detection limit for the method is about 0.1 ppm for ions, in the aqueous extract, with the normal response range being 0.1 to 100 ppm. The relative precision above the 1 ppm level is about 5 percent.

The ionic species fluoride, sulfide, and cyanide are best measured using ion selective electrodes. The ion selective electrode in conjunction with a reference electrode is placed in a quantity of aqueous filter extract. The voltage measured is related directly to the logarithm of the ion concentration. The minimum detection limit for this method of analysis is about 0.1 ppm for ions in the aqueous extract, with the normal linear response range being 0.1 to 100 ppm. The relative precision above 1 ppm is about 5 percent.

D.5 BIOLOGICAL TESTS (MUTAGENICITY)

D.5.1 Laboratory Screening

The Ames screening bioassay test is a method of detecting the presence of mutagenic substances in the ambient atmosphere adjacent to synthetic fuel plants. It is a highly sensitive, reliable, and relatively simple point mutation test with consistent results.

Samples are collected much the same as for particulate organic pollutants and then subjected to an Ames screening bioassay test using the bacteria Salmonella typhimurium as the standard test organism. Detailed information on the sampling and analytical protocols of this method may be found in references D-75 - D-87.

Other possible laboratory screening tests for mutagenicity (employing mammalian cells rather than bacteria) include: a Chinese hamster ovary mutagenesis test using the K1 cell line (which measures point mutation, as does the Ames); and a related Chinese hamster ovary test evaluating sister chromatid exchange, a measure of gross genetic change. More detailed tests for mutagenic activity (e.g., measures of cell transformation) are considered to be beyond the screening bioassay procedures envisioned in this manual.

D-5.2 Possible Field Screening

Since it is not possible to assure that all potentially mutagenic substances emitted from synfuels facilities will be chemically identified, there is a need for an ambient monitoring technique to be used to detect the presence of such substances. The plant Transdescantia paludosa (Spiderwort) in the family Commelinaceae, can be used to detect the presence of mutagens under field conditions. The test is a simple, rapid, inexpensive, and a reliable bioassay technique (D-88 - D-90).

Although the test also can be used in a laboratory to detect mutagens in liquid discharges or ambient water, it is described here within the context of its use in the field to monitor airborne pollutants. Cuttings of the plant can be maintained in tapwater or nutrient solution for year-round growth and reproduction by giving supplemental light during the short-day season of the year. Inflorescences of the plant cuttings can be carried to monitoring sites on and off the synthetic fuel plant site for exposure to the atmosphere for a standard period of time (e.g., 6 hours) prior to fixation in acetoalcohol and storage in ethanol for future preparation of microslides for observation of micronuclei (MCN) development during the early tetrad stage of meiotic development. Field and laboratory controls can be established. Repeated monitoring under different weather and wind conditions can give reference data for a particular site. The appropriateness and effectiveness of this technique for ambient air monitoring has been demonstrated in its use at industrial complexes, public parking garages, truck stops, a bus stop, and an office where smoking occurs (D-88, D-90).

D.6 RADIOACTIVE SUBSTANCES

Because of their sedimentary origin, shales and coals contain trace amounts of radioactivity, notably radionuclides of the Uranium-238, Uranium-235, and Thorium-232 decay chains. Important decay products are Radium-226 found in solid and gaseous samples. Liquid samples should be analyzed for Radium-226 and Radium-228. It is known that some of the radio-nuclides become enriched in coal and shale plant production streams and wastes relative to raw resources. Considerable concern has been expressed that when these wastes are released into the ambient environment (in the atmosphere--mostly associated with airborne particles) there is a potential for radiological impact on humans (D-91 - D-94).

Concentrations of Radium-226 on particulate filters can be determined by Ge(Li) spectroscopy. Along with Radium-226, the important radionuclides of Lead-212, Lead-214, Bismuth-214, Potassium-40 and other elements can be quantitatively measured by this method (D-92, D-95, D-96).

Proportional counters have been used widely for counting filter papers for alpha and beta radiation. Counting of gamma activity usually is performed with a crystal as a scintillation source. If a high reading is observed, the material on the filter can be dissolved and chemically separated to identify particular elements of concern. A good discussion of the use of radiological surveillance as a tool in ambient air pollution monitoring is presented in reference D-95.

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APPENDIX E

AMBIENT WATER MONITORING TECHNIQUES

E.1 SAMPLE COLLECTION AND PREPRATION FOR ORGANIC ANALYSIS

The importance of procedures for collection and preservation of aqueous samples for organic analysis cannot be overemphasized. The sample must be collected so that it is representative of the process or body of water being sampled, and the sample must be presented to preparation and analysis procedures without loss of any of the compounds of interest and without contamination. The choice of methodologies to be employed in collection and preservation of samples must take into consideration the system that is being sampled, the compounds of interest in the sample, and the analytical techniques which will be used to determine these compounds.

E.1.1 Sampling

There are two basic procedures used for aqueous sampling: discontinuous or batch sampling and continuous sampling.

E.1.1.1 Batch sampling--

Batch sampling is probably the most commonly used procedure because it is simple, fast, and requires no specialized apparatus. Usually, the sample container, a glass bottle or jar, preferably amber, is filled with the aqueous sample and capped. If a sample collected by the batch method is to be analyzed for very volatile organic compounds, the bottle must be filled and capped so that there are no air pockets into which the compounds of interest can vaporize (E-1). If headspace analysis is to be used in determining highly volatile compounds, a fixed volume of headspace should remain in the bottles after the samples have been collected. A combined sample collection/storage/purge vessel has been designed for the analysis of volatile organics in sediments (E-2, E-3). Using this approach, losses of volatile components due to sample transfer are eliminated.

Storage conditions can significantly affect analyte recovery during volatile analysis. For samples sealed using Teflon® septa, losses of components were lowest for samples stored without headspace. If headspace is present, losses are minimized by storing the sample inverted. Apparently volatile organics partition into the headspace and then can permeate through the Teflon® septum over time.

Batch sampling for the analysis of moderately volatile compounds is generally carried out by simply filling the sample bottles and sealing with Teflon® lined screw caps. Volatility losses have been reported for C_{12} to C_{18} alkanes during storage using this technique (E-4). A hexane keeper solvent has been used to minimize these losses (E-4, E-5).

There are significant problems associated with the use of batch extraction techniques. Batch sampling increases the probability of obtaining nonrepresentative samples. Analysis of a sample obtained by batch methods provides information about the system only at the point and time at which the sample is taken. Statements made about the system as a whole based on this information may be inaccurate. Pooling, blending, and dividing a number of grab samples or using depth-integrated batch samplers to obtain a sample which is truly representative requires a detailed knowledge of the flow and transport characteristics of the system. For volatile compounds, pooling or blending are unacceptable since significant losses of volatile components may occur during transfer.

E.1.1.2 Continuous sampling--

An alternative to batch sampling is continuous sampling. With this method, a large volume of water is pumped into a sample reservoir or through a column packed with a sorbent material. The sorbent material is commonly activated carbon, resin, or polyurethane foam. Continuous methods allow sampling of larger volumes of water over extended periods of time. Thus, samples collected by this technique are more representative of the system under investigation, and results of the analyses of these samples are not affected by spurious changes in the character of the system under investigation. Additionally, a single time-integrated sample can often be collected and analyzed in lieu of several batch samples to significantly reduce analysis costs (E-6 - E-9). Commercial units, e.g., ISCO, are available for time-integrated, grab sampling.

Disadvantages associated with continuous sampling techniques are that it is time-consuming; it requires specialized (and somewhat costly) equipment, and it is difficult to use if there are space limitations at the sampling site. There is also a greater chance of contamination during a continuous sampling procedure since the sample is exposed for longer periods of time and since there are more equipment surfaces which the sample must contact. Samples collected by continuous methods are subject to losses, degradation, and contamination just as those collected batchwise. Losses are particularly significant for more volatile compounds, and it is difficult to add any type of preservative to a sample which has been collected on a sorbent column.

E.1.1.3 Sample Contamination--

A problem which affects both batch and continuous sampled waters is contamination. Cleanliness of the sample containers and cap is very important if contamination of the sample is to be avoided (E-1, E-10). To check contamination levels, field blanks and laboratory blanks should be run with each set of samples (E-5, E-11). A lab blank is water of known purity which is collected under controlled laboratory conditions and stored in the laboratory. Field blanks are prepared in a similar manner and then subjected to the environment of exposure, handling, shipping, and storing along with the samples. In this way, it is possible to identify and quantify compounds in the sample which are due to contamination.

E.1.2 Sample Preparation

E.1.2.1 Phase Separations--

Environmental waters are not a one-phase system, and, in most cases, aqueous organic contaminants do not exhibit true solution behavior. Rather, the behavior is governed by competitive interactions between phases. In order to adequately sample and analyze water matrices, it is necessary to know the identity of competing phases, their nature, their effect on organics in aquatic ecosystems, and their experimental behavior during analysis. Where possible, all phases of the sample should be extracted. This is possible for solvent extraction techniques. Unfortunately, sorbent columns accumulate only dissolved organics which may introduce an experimental bias.

E.1.2.2 Internal Standard--

In order to assess the degradation of a sample or the loss of compounds of interest, an internal standard or group of standards should be added (E-5, E-11). These are best added to the sample in the field at the time of collection (E-5), but are usually added in the laboratory. The marker compounds should be different from any compounds expected to be in the sample but should be chemically similar to the species of interest so that the fate of the standards mimics the fate of the sample analytes during handling, preservation, transportation, and storage procedures.

E.1.2.3 Preservation--

The immediate analysis of an aqueous sample at the collection site would preclude the need for sample preservation; however, this is impractical for most situations. Preservation of organic samples is a very difficult problem with a limited number of techniques available. Additionally, the requirements of many analytical methodologies impose severe restrictions on the preservation techniques which can be used.

Ideally, preservative would be present in the sample container prior to collection and would disperse immediately, stabilizing all parameters (analytes) for an indefinite period of time. Samples are protected from photodecomposition by using amber glass bottles as sample containers.

Chlorination has been one of the most extensively used techniques for the inhibition of biochemical degradation. Unfortunately, free chlorine is also an active oxidizing agent and readily reacts with substituted aromatics. Thus, the use of chlorine as a preservative is not appropriate when trace levels of aromatic species are to be analyzed (E-12, E-13).

Alternate sterilization techniques and biocides reported for environmental matrices include: (1) mercuric chloride (E-14); (2) formalin or hexachlorophene (E-15); and (3) sodium hydroxide, sulfuric acid or copper sulfate-phosphoric acid (E-16). An alternative to chemical preservation is to seal the sample container and store the sample at as low a temperature as possible.

Another process which can compromise the integrity of an aqueous sample is adsorption of the organic components onto the glass walls of the sample container. This problem is minimized by the addition of a nonpolar solvent such as isooctane, methylcyclohexane, or methylene chloride to the sample container before it is sealed in the field (E-17).

E.2 DETERMINATION OF VOLATILE ORGANIC COMPOUNDS

E.2.1 Static Headspace Analysis

Static headspace analysis is a method for determining volatile compounds in liquids by measuring vapor phase components which are in thermodynamic equilibrium with the sample of interest in a closed system. For aqueous systems, the distribution of sample components between water and gaseous phases depends upon their water solubility and vapor pressure at the equilibration temperature. For example, compounds with a high vapor pressure and low solubility will preferentially partition into the vapor phase.

In static headspace analysis, equilibration is performed in a sealed glass container at a constant temperature. Equilibration time depends upon the sample volume and equilibration temperature and, in most cases, even with large samples does not exceed 60 minutes.

After equilibration, a volume of headspace is injected onto the chromatographic column using a gas tight syringe or a gas sampling loop (E-18, E-19). Since the sample is a gas, a heated injection port is unnecessary making this technique well suited for heat labile compounds. Usually packed column gas chromatography has been used for analysis; however, adaptation to high resolution capillary columns with no loss in quantitative precision and a significant improvement in retention time accuracy and chromatographic separation has been reported (E-20).

Accurate quantitative analysis for the static headspace technique depends upon the calibration procedure. Since the partition coefficient of the solute in the equilibrated gas-liquid system is a function of its activity coefficient, calibration solutions should closely approximate the sample matrix. A standard addition method was developed to calibrate unknown samples (E-20, E-21). As an alternative, hydrocarbons in water were quantitated using multiple equilibrations of the sample with equal volumes of gas (E-22, E-23). Each gaseous extract was analyzed by GC and analyte concentrations calculated by extrapolating the relationship between the peak areas and the number of equilibrations.

Quantitative headspace analysis can be a very accurate procedure. However, good reproducibility depends upon two factors; namely, exact temperature control during equilibration, and a reproducible method for transporting and injecting the headspace sample into the gas chromatograph. Results with a commercial headspace sample accessory have given precisions of 0.8% as a coefficient of variation (E-24). A precision of ±5% was reported for the analysis of halocarbons in drinking, surface, and wastewater samples (E-18).

Detection limits for static headspace analysis depend upon: compound type, GC detector, and conditions for equilibration. The following table summarizes reported detection limits under a variety of test conditions.

Any compound which will give a vapor pressure over its aqueous matrix can be analyzed via static headspace analysis. Obviously, the higher the vapor pressure, the more suitable the technique. Low molecular weight, low boiling point, hydrophobic compounds are best suited. Vapor phase partitioning for the following chemical classes followed the order: alkanes > olefins > cycloalkanes > aromatics. Within each chemical class, an increased vapor partition was observed as the molecular weight decreased. With salting-out and sufficiently high equilibration temperatures, water soluble compounds including methanol, ethanol, acetone, and methyl ethyl ketone are also amenable to analysis (E-25). However, use of elevated temperatures during equilibration may prevent the analyses of heat-sensitive compounds.

E.2.2 Purge and Trap

The most widely used method for isolating volatile organic materials (boiling point <200°C) from water is to purge the sample with prepurified gas, collect the stripped materials on a sorbent trap, and analyze the trapped compounds by thermal desorption followed by gas chromatography or gas chromatography/mass spectrometry. Alternatively, for samples which tend to foam, the sample headspace may be purged instead of the sample itself.

Removal of organic compounds from water by sparging with an inert gas is frequently referred to as volatile organic analysis (VOA) or purge and trap. The technique depends upon partitioning of the compounds between the aqueous and gaseous phases. This partitioning is a function of water

Table 1. DETECTION LIMITS FOR STATIC HEADSPACE ANALYSIS

Compound or Compound Class	Equilibration Condition	Pre-Concentration	Detector	Detection Limit	Reference
Chloroform	90°C, 45 min no salt	None	ECD	1 ppb	E-26
Sulfides, carbonyls, esters	Na_2SO_4	None	FID	10 ppb	E-25
Halogenated aliphatics	3.35M Na_2SO_4, 50°C	None	ECD	1 ppb	E-27
Methanol	Na_2SO_4	None	FID	1 ppm	E-25
Methanol, ethanol, acetone	70°C, Na_2SO_4	Distillation	FID	4 ppb	E-26
Methyl ethyl ketone	70°C, Na_2SO_4	Distillation	FID	8 ppb	E-26
Halogenated aliphatics	80°C, no salt	None	FID	1-5 ppb	E-28
Hydrocarbons	—[a]	None	FID	100 ppm	E-22
Hydrocarbons	40°C, no salt	None	FID	2 ppb	E-21
Benzene	40°C, no salt	None	FID	100 ppb	E-20
Chloroform	0.1N $Na_2S_2O_3$, 50°C	None	FID	1.5 ppb	E-29
Vinyl chloride	—	None	FID	5 ppb	E-30
Hexachloroacetone, hexafluoroacetone	—	KOH hydrolysis	FID	10 ppb	E-31

[a] Exact conditions unknown.

temperature, gas-water interfacial area, and the water solubilities (<2%), volatilities (<200°C), and aqueous activity coefficients of the test compounds. In addition, the partition rate depends on the flow rate and total volume of the purge gas.

The assembled purge apparatus consists of a container with a purge gas inlet, a device for regulating sample temperature, and a purge gas outlet through a sorbent cartridge (E-32 - E-34).

The cartridge is composed of material with a high affinity for organic compounds, and preferably, a low affinity for water. Tenax GC® is the most commonly used trapping material. It is thermally stable, contains few background contaminants, provides few sites for irreversible adsorption, is chemically inert, and has a low affinity for water. Its major drawback is its low affinity for a number of very volatile organic compounds including the lower alkanes and methanol (E-35). Alternate sorbents have also been employed. EPA Method 624 for the analysis of volatile organics currently uses a silica gel/Tenax® trap (E-36).

Sample volumes vary from 0.5-1000 mL depending upon the type of sample and concentration of the substances to be determined. Gas flow rates range from 20-200 mL/min and purge times from a few minutes to several hours depending, again, upon the sample concentration and the appropriate breakthrough volume for the target analyte on the sorbent cartridge.

There are a number of considerations involved in determining purge temperature. Even though maximum stripping occurs at 90-98°C, these elevated temperatures may cause problems with condensation on the trap material, artifact formation, and thermal decomposition. Furthermore, samples which tend to foam do so to a greater degree at higher temperatures. For these reasons, analysis of low molecular weight, hydrophobic compounds is performed at ambient temperatures. Compounds with boiling point less than 200°C and aqueous solubilities less than 2% are amenable to this type of analysis. Elevated temperature purge and trap techniques have been reported for a number of volatile polar organic compounds (E-5, E-37 - E-39). Recoveries of many of these compounds improved significantly with the addition of salt to the aqueous solution prior to analysis (E-37).

Analytes trapped on the sorbent cartridge are introduced into the chromatographic system using thermal desorption. At this point test components may be either focused in a cryogenic trap (E-39) or transferred directly to the GC column (E-36). For packed column analysis the latter approach is generally used. The purge and trap technique can be performed with the cartridge directly on-line to the gas chromatograph and detector system.

For the separation of volatile organics, both capillary (E-39) and packed (E-36) columns have been used. Chromosorb 101, Carbowax 1500 and 20M, SE-30 and OV-101 are the most frequently used liquid phases for GC analysis. Fused silica capillary columns with bonded phases have become popular for all GC analysis including the analysis of volatile compounds. However, the use of an on-line purge and trap system interfaced to a capillary column causes several difficult problems. During capillary column chromatography the sample components must be introduced onto the column as a sharp band to avoid deteriorating chromatographic resolution. This may be achieved by cryotrapping using either a cryofocusing unit (E-39) or by cooling a small portion of the capillary column to liquid nitrogen temperatures (E-40). Unfortunately, the volume of water collected on the trapping material is often large enough to cause freezing during the focusing procedure. The use of a water cooled condenser or a condenser tube to remove water from the gas stream prior to the sorbent cartridge has been reported (E-41). A dry purge of the sample cartridge to remove water after the load operation has also been reported (E-39, E-42). Other researchers have split the gas stream after desorption to minimize the amount of water entering the chromatographic system (E-43). However, this significantly decreases method sensitivity.

E.2.3 Closed-Loop Gas Stripping

The closed-loop gas stripping technique involves continuous gas stripping of water samples followed by trapping on a small activated carbon filter. This can be done by either stripping at 30°C using the headspace gas to purge the sample, or stripping with water vapor by boiling the sample in a closed-loop system (E-44, E-45). A modified version purges the aqueous sample rather than the sample headspace (E-46, E-47). The continuous purge and trap apparatus is constructed entirely of glass or glass and stainless steel to minimize surface contamination.

For ambient stripping, a water sample of 0.5-2.0 L is carefully introduced into a 1 or 5 L glass bottle equilibrated at 30°C, and connected to the closed-loop system. An adsorbent filter constructed of 1.5-5.0 mg heat-activated wood charcoal collects organics in the stripping loop. Stripping is initiated at 1.0-2.5 L/min for 1-3 hours by activation of a stainless steel bellows pump. During the process, stripping gas is warmed to approximately 40°C just prior to the carbon filter to minimize adsorption of water vapor and hence restriction of flow through the filter.

Extraction of the exposed carbon filter can be effected in two ways: If only volatiles are desired, the filter can be analyzed by thermal desorption directly onto the gas chromatographic column (E-48). Extraction of less volatile compounds from the filter involves careful elution with 5-15 μL of purified and redistilled carbon disulfide (E-49, E-45). In cases where heavily contaminated water has been purged, 10-100 μL methylene chloride has been used (E-50). Component identification as well as quantitative analysis are performed by gas chromatography/mass spectrometry (GC/MS) without further concentration.

Due to the number and diversity of compounds which may be collected on the charcoal filter, glass or fused silica capillary GC columns are recommended, although packed columns should provide sufficient resolution for clean water samples.

No inherent difficulties are associated with mass spectrometric detection in conjunction with closed-loop gas stripping analysis. In every reported instance a mass spectrometer was employed as a detector, presumably because of its utility in identifying components of complex mixtures.

E.3 DETERMINATION OF EXTRACTABLE ORGANIC COMPOUNDS

E.3.1 Liquid-Liquid Extraction

Liquid-liquid extraction (LLE) is a widely employed method for concentrating semivolatile nonpolar organic compounds from water samples. If the analyte of interest has a higher affinity for the extracting solvent than the sample matrix, then it will partition into the solvent. The affinity of an analyte for the solvent is defined by the distribution coefficient (K_D) using this parameter, the percent of analyte extracted into the solvent phase (%E) can be calculated by (E-5]):

$$\%E = \frac{100\ K_D}{K_D + \frac{Vw}{Vo}}$$

where Vw and Vo are the volume of water and organic solvent used during extraction. From this equation it is obvious that high analyte recoveries during LLE depend upon either a large distribution coefficient or a small water:solvent ratio.

The choice of solvent is critical to LLE procedures. As discussed above, the solvent must have a large distribution coefficient for the compounds of interest. Extensive listings of partition coefficients are available for various solvent systems (E-51). Partition coefficients for all organic compounds are higher for neutral species than for compounds with an electrostatic charge. To achieve electrostatic neutrality, acids are extracted at a low pH. Conversely, bases are extracted at an alkaline pH.

Along with having a high extraction efficiency for the analytes of interest, the extracting solvent should be immiscible with the sample, not contain contaminants which might compromise subsequent analysis, be chemically inert, be specific for the compounds of interest, and be amenable to the analytical method of choice. Since solvent evaporation is usually employed to further concentrate sample extracts, solvents with low boiling points are preferred. Benzene (E-52, E-53), toluene (E-54), pentane (E-55), hexane (E-56, E-57), and methylene chloride (E-54) are routinely used to extract hydrophobic compounds from water. Chloroform (E-58, E-59), ethyl acetate (E-60, E-54), diethyl ether (E-61), methyl _t_-butyl ether (E-62, E-63), and isopropyl ether (E-64) have been used to extract more polar analytes.

The addition of salt to the aqueous matrix will increase the activity coefficients of organic analytes to effectively increase the partition coefficient into the organic solvent. Sodium sulfate (E-65, E-66) and sodium chloride (E-62, E-63, E-65) are most commonly used to achieve salting-out. Unfortunately, the addition of salt increases the density of aqueous solutions which may promote emulsion formation when heavier-than-water solvents are used for extraction. This is significant since methylene chloride is commonly used as an extracting solvent.

In practice, LLE procedures are of two types, batch and continuous. Batch extractions are generally carried out by thoroughly mixing the sample and extracting solvent in a separatory funnel. The two phases are allowed to separate and the organic layer is removed. For separatory funnel techniques two minutes of vigorous shaking is usually sufficient to obtain equilibrium partition between the phases. Samples which tend to emulsify are often extracted using gentle mixing over a longer time period. For separatory funnel techniques, heavier-than-water solvents are preferred for easy handling. Exhaustive extraction procedures can involve extracting 1 L aqueous sample as many as three times with 200 to 250 mL of organic solvent each time (E-63). The use of large solvent volumes is essential for polar compounds with low affinity for organic solvents; i.e., amines, alcohols, hydroquinone, phenols, and nitro compounds. But the use of large solvent volumes has several disadvantages (E-66): a concentration step is required to remove most of the solvent to improve sensitivity; impurities in the solvent are also concentrated during the concentration step; the more volatile compounds may be lost during evaporation; contamination and sample losses are more probable because of handling and transfers; and the cost of analysis increases because more solvent is used and the concentration step adds to the time per analysis. For compounds which partition readily into organic solvents these problems can be circumvented using microextraction techniques. Typically, sample to solvent ratios of 100 to 500 with total organic solvent volumes of 100 to 1000 μL have been used. This technique should be applicable to analyzing hydrophobic compounds in water samples. However, special vessels are required, more aggressive shaking is necessary to establish equilibrium, only lighter than water solvents can be used and problems with phase separations may be more severe for small solvent volumes (E-66).

The Environmental Protection Agency has developed a series of extraction procedures which use gas chromatography with specific detectors or HPLC for the measurement of specific organic materials. Test organics were divided into several classes based on chemical structure and specific methods were then developed for extraction, cleanup, and detection of these analytes. Of these methods, only Method 610 for polynuclear aromatic hydrocarbons is applicable for the range of compounds expected to be found in synfuel wastes (E-67).

EPA Method 625 (E-68) uses extraction with methylene chloride and analysis by GC/MS to quantitate priority pollutants in wastewater samples. Recoveries for these compounds are generally greater than 70% with a limit of detection of 10 ppb. Although the method has not been tested for many of the compounds expected in synfuel waste (i.e., aldehydes, thiophene, basic nitrogen containing compounds, nitrogen heterocycles, and weakly acidic phenols), precision and accuracy of the method should be acceptable. Poor recoveries can be expected for the carboxylic acids, alcohols, and the dihydrophenols due to poor partitioning into the extracting solvent. Poor recoveries for the alkanes and alkenes will probably result from volatility losses during storage and transfer. In addition, weak acids such as phenol and cresol tend to partition into both fractions, to give low recoveries in any single fraction. The use of mass spectrometry verifies compound identification and may reduce interferences during quantitation. However, for complex water sample, packed column chromatography may not provide sufficient resolution for either quantitative or qualitative analysis. No cleanup procedures have been given for use with very complex samples.

Using the Master Analytical Scheme for the analysis of organics in water, two separate water samples are extracted and analyzed. One sample which is extracted at pH 8 with methylene chloride will contain basic, neutral, and weakly acidic compounds (E-5). The second sample which is extracted at low pH with methyl-t-butyl ether will contain strong acids. This method has been tested and used for the analysis of a range of extractable organic compounds, including alkanes, PNAs, alcohols ($>C_{10}$), ketones, phenols, thiophenes, basic N-containing compounds, nitrogen heterocycles, and carboxylic acids. Recoveries for most compounds are greater than 60% with a limit of detection of approximately 10 ppm. The use of a keeper solvent prevents volatility losses for the alkanes and alkenes. Use of methyl-t-butyl ether as the extracting solvent improves extraction efficiency for the carboxylic acids. The use of capillary column chromatography, and sample cleanup procedures help to minimize interference during analysis.

E.3.2 Sorbent Columns

The use of sorbent columns in determining organic compounds in water is an application of liquid-solid chromatographic techniques (LSC). Compounds are isolated from the aqueous matrix by adsorption onto a solid phase which is composed of small particles of commercially available materials, including carbons, resins, and foams.

Sorbed analytes are eluted from the solid phase with a solvent or solvent mixture for which they have a high affinity. Solvents such as methanol (E-62, E-69) ethanol (E-70), acetone (E-71, E-72), diethyl ether (E-71, E-73), acetonitrile (E-74), chloroform (E-72, E-75), and methylene chloride (E-62) have been used either alone or as solvent mixtures. Water at an alkaline pH (E-76) or weak organic bases (E-77) have been used to recover organic acids from resin columns. Alternately, thermal desorption has been used to recovery analytes from a number of sorbent materials. This technique is most commonly applied to Tenax GC®, but has also been reported for XAD resins (E-78, E-79).

A method using 12 L water sample concentrated on XAD-4 resin has been tested and used for the analyses of phenols, PNAs, alcohols ($>C_{10}$), ketones, thiophenes, basic N-containing compounds and nitrogen heterocycles (E-5). Recoveries for most compounds are greater than 60% with a limit of detection of approximately 0.5 ppm. Recoveries of alkanes and some PNAs is low due to volatility losses during storage and column accumulation procedures. This method should only be used for sample waters containing low levels of particulates to prevent clogging the resin column during sample processing.

E.4 DETERMINATION OF INTRACTABLE ORGANIC COMPOUNDS

Intractable organics are defined as those compounds which are polar and water soluble and, therefore, are not easily concentrated from water using either purging or extraction techniques.

E.4.1 Direct Aqueous Injection

The easiest approach for measuring intractable organics is simply to analyze them in the water sample without preconcentration. Analysis of organic compounds in water by direct aqueous injection (DAI) involves analysis in an aqueous medium, by gas-liquid or gas-solid chromatography. Injection volumes, which are typically 1-50 μL, have been used for the determination of volatile organics in various waters.

Chromatographic separation is achieved using a variety of solid supports such as Tenax GC®, Chromosorb 101 (E-80, E-81) or Porapak Q (E-81 - E-84). Separations involving compounds with amino functional groups have been done on columns containing Carbowax 1500 (E-85) or Pennwalt 223 plus 4-7% KOH (E-86) to minimize peak tailing. Similarly, Apiezon L has been used to determine N-nitrosamines (E-87). Manufacturers' literature for some fused silica capillary columns indicate good performance using the DAI technique. However, some initial work has reported problems with poor peak shape and poor reproducibility for both peak area and retention time for a number of low molecular weight polar compounds (E-88).

The lack of sample preconcentration in DAI necessitates that optimal sensitivity be achieved during detection. Flame ionization detectors are useful only when the component concentrations are quite high (~0.1 ppm), as is the case with most energy effluents and wastewaters. Electron capture or Hall electrolytic conductivity detection does possess sufficient sensitivity to detect halogenated hydrocarbons at levels found in drinking waters. Mass spectrometry affords sensitive and selective detection for DAI only when operated in the selected ion monitoring mode. Compatibility of DAI with MS is facile, requiring only that the elution of water from the chromatographic column not coincide with the elution of other sample constituents.

For nonvolatile organics, detection limits may be decreased by concentrating the water sample (E-89). Recoveries of ~70% were achieved for acrylamide spiked into water samples using this procedure. Limits of detection are approximately 50 ppb for GC/MS, and 10 ppb for GC/FID, and 1 ppb for GC/NPD. Other amides likely to be found in synfuel waste could also be analyzed by this procedure.

E.4.2 Ion Exchange

Ion exchange is an adsorption process involving the displacement of resin ions by solute ions of similar charge. Functional groups on the surface of a solid sorbent provide sites for electrostatic exchange (E-90). Theoretically, ion exchange processes should remove any ionic species from an aqueous solution making ion exchange a valuable technique for concentrating charged polar organics or removing inorganic ion interferences from environmental water samples.

Generally, an ion exchange resin consists of a hydrocarbon backbone with soluble ionic functional groups attached. The concentration of ionic groups within the resin determines exchange capacity, while the chemical nature of the groups effects both ion exchange equilibrium and general ion selectivity (E-91).

During concentration, an aqueous solution is passed through the resin column, allowing exchange to take place. Adsorbed ions are then eluted either by neutralizing the charge on the solute or by rinsing the column with a highly concentrated solution of counterions (E-90). Eluting solutions for organic acids have included HCl in methanol (E-92, E-93) HCl in diethyl ether (E-94), and $NaHSO_4$ in a mixture of water/acetone or acetonitrile/acetone (E-93, E-95, E-95). Organic bases have been eluted with KOH in acetonitrile.

In highly saline solutions, resin capacity may be quickly saturated with inorganic ions to give low and variable recoveries for the organics of interest (E-97).

An anion exchange procedure was developed for the analysis of low molecular weight carboxylic acids (E-5). Recoveries greater than 60% have been reported for the C_3 to C_9 acids with a limit of detection of approximately 1 ppm using a 3 L sample. The use of capillary column chromatography and ion exchange concentration helps to minimize interferences during analysis.

E.5 DETERMINATION OF INORGANIC SPECIES

The metals and ions found in surface and ground waters can be determined by those same methods used to analyze extracts of particulate material (E-98, E-99 - E-102). Spark source mass spectrometry is a suitable technique for elemental screening (E-103 - E-105) while atomic absorption spectrometry (E-106 - E-108) or inductively-coupled argon plasma emission spectrometry (E-109, E-110) are best for accurate and precise monitoring of metals.

Ion chromatography (E-111, E-112) and ion-specific electrodes (E-113) are the best methods for measurement of ions in the water samples.

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APPENDIX F

AMBIENT SOIL MONITORING TECHNIQUES

F.1 SAMPLE COLLECTION AND PREPARATION FOR ORGANIC ANALYSIS

The aim of any sampling procedure is to ensure that the sample is entirely representative of the environment from which it was taken and that the sample maintains its integrity until extraction and analysis. Procedures for sampling should address sample collection, sample preservation, and preparation of sampling devices and containers to avoid contamination.

F.1.1 Sample Collection

Because soils, sediments and sludges are poorly mixed matrices and because collection is restricted to discrete grab samples, special attention must be given to obtaining a representative sample. The generally accepted method for accomplishing this is the sample compositing method. The exact design of such a method depends on many factors such as sample material, source and rate of natural and anthropogenic inputs, and the information desired. Guidance in the design of the sampling protocol can be obtained from the Handbook for Sampling and Sample Preservation of Water Wastewater (1976) and the NPDES Compliance Sampling Inspection Manual (1977). The aid of statisticians may be required to effectively apply these principles to a given sampling situation. In general, multiple grab samples are taken from regular locations on a sampling grid, and composited. If information about recent deposition in the soil is desired, then the sample is scraped from the top few cm of the surface. On the other hand, if a history of the substrate is desired, then core sampling is used. This can be accomplished by a simple bulb-planter or by a more elaborate drilling device depending on the depth of sample desired (F-1).

F.1.2 Sample Handling and Preservation

Losses of organic compounds during handling and storage of soil samples may occur due to volatilization, adsorption, or chemical, bacterial or photodecomposition.

Samples can be protected from photodecomposition by using amber glass bottles as sample containers or alternatively by wrapping the container carefully with aluminum foil.

Musterman and Morand report the effective preservation of sludge from bacterial decomposition with formaldehyde (F-2). Bacterial decomposition may also be prevented by the addition of mercuric chloride (F-3), formalin (F-4), or hexachlorophene (F-4). A more prevalent method for avoidance of bacterial degradation is sample storage at 0° or 4°C until analysis (F-5). Maienthal and Becker report the storage of samples at -70° to -80°C to prevent the biological breakdown of certain pesticides (F-6). Adsorption of organic components onto the glass walls of the sample container may be minimized by the addition of a nonpolar solvent to the sample container before it is sealed in the field (F-7). The addition of certain quenching agents to the sample inhibit further formation or organochlorine compounds by reducing free chlorine. Sodium thiosulfate (F-8), sodium sulfite (F-9), potassium ferrocyanide (F-10), and ascorbic acid (F-11) are commonly used in this application. Drying of samples prior to analysis should be approached with caution as losses of pesticides have been reported via this process (F-12).

In general, the use of preservation methods has been reported for individual compounds or compound classes. Their applicability to compounds of interest to the synfuel industry must be evaluated prior to use.

F.1.3 Materials, Purity and Cleanliness of Sampling Equipment

Careful selection and cleaning of sampling equipment and containers is necessary to prevent contamination, degradation or adsorption of the sample and its components. The choice of construction materials for equipment is further dictated by the need for ruggedness and ease of cleaning in the field.

Rubber, neoprene, vycor, polyvinyl chloride, polystyrene, glass, polypropylene, linear polyethylene, platinum, etc., have been found to cause contamination of samples for organic analysis. Stainless steel, glass, FEP Teflon and aluminum foil are recommended for sampling (F-6). Contamination of all types of samples for trace organic analysis by plastics and plasticizers has been well documented (F-13). Persons involved in sampling, sample handling and analysis should be constantly alert for possible contamination from this source.

Much diversity exists in methods used for cleaning glass containers and equipment (F-14, F-15). Nonglass sampling equipment should be vigorously scrubbed and thoroughly rinsed with water between uses. While a thorough scrubbing with hot detergent solution followed by rinsing with deionized water and solvent might seem a prudent choice, the probable need for repeated use of samplers in the field may well make this impractical. Whatever the method chosen, its effectiveness should be demonstrated by the regular analysis of field blanks.

F.2 DETERMINATION OF EXTRACTABLE ORGANIC COMPOUNDS

Analytical methods for the determination of organics in soil are basically three-step procedures: (1) extraction and isolation from the sample matrix (both aqueous and solid); (2) fractionation or cleanup of the sample extracts; and (3) analysis of sample fractions. Currently, there are no standardized methods for analyzing organics in soils. Further, since soils are complex matrices which can undergo multiple interactions with organic compounds, the "best" method for analysis may vary from sample to sample. Comparisons of methods has been made by assessing recoveries for organic analytes spiked into solid matrices. Unfortunately, this approach does not always provide meaningful information, since samples spiked with test compounds will not necessarily reflect extraction behavior of soils. Alternately, recoveries of standards from spiked sample extracts, and inter- and intralaboratory comparisons of test methods applied to reference samples have also been used. The majority of this research has been applied to the analysis of hydrocarbons and polynuclear aromatics (PNAs) in sediments. With only a few exceptions, soils should behave in a manner similar to sediments, and although the nitrogen- and oxygen-substituted aromatic hydrocarbons of interest to the synfuels industry are more polar compounds, many of the procedures should also be applicable directly or with slight modifications to their analysis. A brief description of the analytical procedures follows.

F.2.1 Extraction/Isolation Procedures

For the analyses of soils or sediments, it is necessary to isolate the organic compounds from both the solid matrix and the water associated with that matrix.

Water removal procedures are extremely important for sediment samples which always have a high water content, and are also important for soils which may contain significant amounts of water when fully saturated. Using the most common procedures, water is removed either before extraction, i.e., air drying (F-16), freeze drying (F-16, F-17), or rinsing with a water miscible solvent (F-18, F-19), during extraction, i.e., adding a desiccant to the sample matrix (F-20), or after extraction, i.e., partitioning the extracts with a water immiscible solvent (F-21, F-22). Air drying or liophilization may cause losses of volatile organics (F-16). However, with the exception of the pyridines, most of the target compounds should be sufficiently nonvolatile for adequate recoveries. Dewatering with a water miscible solvent may extract the more polar organics. For example, significant losses (>30%) were reported for nitrobenzene, phenol, and decanol during rinses with methanol and acetonitrile (F-23). Many of the target compounds should be sufficiently hydrophobic to minimize this type of loss. Solvent partitioning of the sample extract with a nonpolar solvent also may result in losses for polar organics.

Extraction of organics from the solid matrix occurs when the solvent is brought in contact with the soil sample. If the analyte of interest has a higher affinity for the extracting solvent than the sample matrix, then it will partition into the solvent. The percent of analyte extracted into the solvent phase (%E) can be calculated by:

$$\%E = \frac{100\ K_D}{K_D + \frac{W_S}{W_0}}$$

where K_D is the distribution coefficient of an analyte between the solvent or solvent mixture and the solid matrix and W_S and W_0 are weights of the matrix and solvent, respectively. Operationally, there are a number of ways in which solvents may be physically brought into contact with the solid matrix including mechanical shaking or stirring, Soxhlet extraction, refluxing, and ultrasonication. If equilibrium is achieved during extraction, then K_D should be the same for all method and differences in extraction efficiency would then be a function of the volume of solvent used during extraction. However, for complex soil samples, it may be difficult to reach an equilibrium state and difference between methods, for the same solvent systems is then a function of how rapidly the partitioning may proceed.

F.2.2 Soxhlet Extraction

The most common method for extraction soils and sediments is Soxhlet extraction. During extraction the sample is placed in a thimble in the Soxhlet tube, solvent evaporates from a boiling flask, condenses, and passes through the sample. This sample extract then returns to the solvent pot. When operated over an extended time period (4-48 h), Soxhlet extraction provides a large volume of solvent for extraction. Soxhlet extraction has the dual advantage of leaving the sample cool and providing multiple extractions over an extended period of time. However, some sediments and clay soils are difficult to extract especially when wet because they agglomerate into a single mass and the solvent does not penetrate. This effect may be reduced by adding inert amendments such as sand, sodium sulfate, or Celite to the sample.

Soxhlet extraction with benzene and methanol has generally been considered the most efficient technique for extracting hydrocarbons (F-23 - F-26). Recently, toluene has been substituted for benzene to avoid contact with a carcinogenic solvent. Solvent systems using methylene chloride/benzene (F-18), methylene chloride (F-17, F-27, F-14), hexane/acetone (F-28, F-29), and diethyl ether/petroleum ether (F-28, F-30) have also been used to extract both soils and sediments with good recoveries for a range of nonpolar and semipolar compounds. Several different methods of extraction have been compared to Soxhlet extraction, including ultrasonic treatment with acetone as the solvent and extractive steam distillation (F-29). All of the methods were quantitative for the spiked sediment. The recoveries were different when a weathered sediment was used with Soxhlet extraction being superior to the other methods.

Careful choice of solvents and extraction conditions are necessary to prevent artifact formation. In situ methylation of acids occurred during Soxhlet extraction of sediment samples using methanol/toluene, whereas Soxhlet extraction with diethyl ether caused formation of benzyl ethers (F-27).

F.2.3 Shaking or Tumbling

Methods which use shaking or tumbling as an extraction procedure are performed by adding the solid matrix and the extracting solvent to a closed vessel, mixing for a specified time period and decanting the solvent. Sequential extractions are usually performed to increase both solvent recovery and extraction efficiency.

Mechanical shaking or stirring at room temperature adds little energy to the sample during extraction and, therefore, minimizes the potential for artifact formation. However, shaking sediment samples with various solvents can produce stable emulsions (F-18). As an alternative, tumbling procedures have been employed which provide gentler mixing. Shaking or tumbling procedures can reduce the time and space required for analyzing multiple samples compared to solvent extraction techniques.

According to some reports tumblings provide extraction efficiencies as high as Soxhlet techniques (F-24). Conversely, significantly reduced recoveries (17-33%) have also been reported (F-21). In a comparison of extracting solvent, hydrocarbon extraction efficiencies were 2-3 times better when methanol was used as a cosolvent for wet sediment (F-18, F-19). Apparently, methanol helps to remove water from the soil or sediment which then promotes better extract efficiency for water immiscible solvent. A number of nonpolar neutral compounds have extracted from soil with a variety of solvent systems: ethanol/acetone (F-31), hexane/acetone (F-32), toluene/acetone (F-32), and toluene/ethyl acetate (F-32).

F.2.4 Ultrasonic Extraction/Homogenization

These techniques rely upon ultrasonic energy to break the solvent-sample interface into the smallest droplets/particles possible, such that contact between the sample and solvent is maximized. During extraction the solid matrix plus desiccant is added to an open extracting vessel with the solvent. Sonication is then performed for a very short period of time (less than 1 h).

Depending on the solvent system, separation of the sample and solvent after treatment is accomplished by centrifugation or filtration. Some solvents, such as dichloromethane do not mix well with the solid matrix and will separate without aid. A variety of polar and nonpolar solvents have been used with this technique with good extraction efficiency (F-26, F-33, F-34).

F.2.5 Fractionation/Cleanup Procedures

Soil samples may contain complex mixtures of both naturally-occurring and anthropogenic compounds which make it difficult to identify, and quantify individual compounds. Even with the use of high resolution capillary chromatography, interferences still occur which require some form of prefractionation in order to reduce the number of compounds which must be resolved during the final analytical step and to remove extraneous background interferences.

Solvent partitioning and open column chromatography are the two most common procedures used and will be discussed briefly.

F.2.6 Solvent Partitioning

Solvent partition depends upon the preferential distribution of solute into one of two intermittently contacted but immiscible liquid phases with compound polarity providing the basis for separation. For ionic species, solute solubilities may be altered by controlling the pH of the aqueous phase as in the familiar acid/base wash sequence. Although solvent partition provides some sample fractionation, additional clean-up methods are usually required prior to final analysis.

The simplest form of solvent extraction fractionation is used when a sample has been extracted with a polar or semipolar solvent. Under these conditions, the addition of water plus a nonpolar solvent to the sample extract will separate nonpolar neutrals from polar neutrals and ionic organics. A number of solvent fractionation schemes have been applied to isolated polynuclear aromatics (PNAs) and aliphatic hydrocarbons from soil, and sediments extracts (F-22, F-34, F-35). In most cases, the extract is first cleaned up using open column chromatography, then the fraction is partitioned between two immiscible solvents to separate the more polar PNAs from the hydrocarbons. The most commonly used solvent systems include: cyclohexane/nitromethane; pentane or hexane/dimethyl sulfoxide; and isooctane/dimethyl sulfoxide.

F.2.7 Column Chromatography

Some form of open tubular column chromatography has been incorporated in most fractionation procedures for soils and sediments. Normal phase chromatography is currently the most common separation mode in general use and is characterized by a polar stationary phase and a relatively nonpolar mobile phase. Where the solid support functions as the stationary phase, the technique is termed adsorption chromatography. Retention and selectivity result from the degree and types of interactions which occur between the polar functional groups of eluting components and the active sites (hydroxy, Lewis acid, ether) on the surface of the support. These factors are easily controlled by proper adjustment of such mobile phase characteristics as dielectic constant, polarizability, hydrogen bonding and ¶-bond interactions. Only a few supports have shown much utility for fractionation of the broad range of organic compounds found in environmental matrices: (1) silica; (2) alumina (acidic, neutral, basic); and (3) Florisil (magnesium silicate).

Table 1 compiles a representative listing of applications reported in the literature. Information on sample matrices, compounds, chromatographic adsorbents, elution patterns and compound recoveries has been included where available. Data in the table demonstrate the applicability of column chromatography to sample fractionation techniques. In addition, an extrapolation to generalized operating parameters may be made using information on elution patterns and solvent systems.

Gel permeation chromatography (also referred to as GPC, size-exclusion, or molecular sieve chromatography) differs from other chromatographic modes in that retention is controlled solely by the molecular size of the eluting species relative to the size of the pores in the support and interaction between the eluting sample components and the support is undesirable.

Open-column GPC has been extremely useful in removing high molecular weight interferences (e.g., humic acids, lipids) from environmental samples prior to analysis by GC, GC/MS or HPLC (F-22, F-34).

Table 1. OPEN COLUMN CHROMATOGRAPHIC SYSTEMS USED FOR FRACTIONATING ENVIRONMENTAL SAMPLES

Matrix	Adsorbent	Elution Pattern	Compounds	Recoveries	References
Distillation extract from crop material	Florisil	1) Hexane: diethyl ether (9:1) 2) Hexane: ethyl acetate (19:1)	1) Chlorinated hydrocarbon pesticides 2) 2,4-D, 2,4,5T	1) – 2) 70 - 90%^{a} 2)	F-36
Soil	Florisil (3% H_2O deactivated)	1) Pentane 2) 6% Ether in pentane 3) Ether	1) – 2) Lindane 3) –	90%b – –	F-37
Sediments	Silica gel	1) –	1) Saturated hydrocarbons, PAHs	–	F-19
Sediments	Alumina-neutral (9% H_2O deactivated)	1) Hexane	1) Chlorinated pesticides	–	F-38
	Silica gel (3% H_2O deactivated)	1) Hexane 2) Benzene	1) Aldrin, PCBs, PCNs 2) Chlordane, DDD, DDE, DDT, heptachlor, lindane, toxaphene	} 85 - 100%^{b}	
Mussel tissue sediments seaweed	Florisil (5% H_2O deactivated)	1) Toluene	1) Hydrocarbons and PAHs	1) 90%^{b}	F-39
Sediments	Silica gel	1) Petroleum ether 2) Methylene chloride in petroleum ether	1) Hydrocarbons 2) PAHs	– –	
	Alumina: silica gel (3:1)	1) Hexane 2) Benzene 3) Methanol	1) Hydrocarbons 2) PAHs 3) Polar neutrals	– – –	
	Alumina: silica gel (1:1)	1) Heptane 2) Benzene	1) Hydrocarbons 2) PAHs	– –	
	Alumina: silica gel (1:2)	1) Hexane 2) Benzene	1) Hydrocarbons 2) PAHs	– –	F-40
Sediments	–	1) Isooctane 2) Isooctane: benzene (1:1) 3) Benzene: ethyl acetate (1:1) 4) Benzene: methanol (1:1)	1) – 2) PAHs, BHC 3) Acetophenone derivatives, phthalates, sterols 4) Polyethylene glycol compounds		

(Continued)

See footnotes at end of table.

Table 1 (continued)

Matrix	Adsorbent	Elution Pattern	Compounds	Recoveries	References
Soil and soybeans	Silica gel	1) 1% methyl acetate in methylene chloride	1) Dioxin	1) 25 to 100%[b]	F-41
Soil and sediment	Alumina: silica gel (1:1)	1) Methylene chloride in pentane (4 to 100%)	1) PAHs fractionated	1) 97%[b]	F-22
Soil and sediment	Florisil	1) Ethyl ether in petroleum ether (5, 15, and 50%)	1) Neutral priority pollutants	–	F-42
Sediment	Alumina	1) 20 mL hexane 2) 20-35 mL hexane 3) 35-50 mL hexane	1) PCBs, PCNs, aldrin, chlordane, DDD, DDT, heptachlor, lindane, toxaphene 2) Dieldrin, endrin, heptachlor epoxide 3) Ethion, malathion, methyl parathion, parathion	– – –	F-43
	Silica gel	1) Hexane 2) Benzene	1) PCN, PCBs, aldrin 2) Chlordane, DDD, DDE, DDT, heptachlor, lindane, toxaphene	– –	
Soil	Florisil	1) Acetone in diethyl ether (4%) 2) Acetone in diethyl ether (50%)	1) Aldicarb sulfonitrile, aldicarb sulfone oxime 2) Aldicarb sulfone	>90%[b]	F-44
Sediment	Silica micro-column	1) Hexane 2) Methylene chloride 3) Methylene chloride: methanol (1:7)	1) Hydrocarbons, pristane, phytane 2) Alkylated benzenes, PAHs 3) Ketones, alcohols, phenols, fatty acids	– – –	F-45
Soil	Florisil (3% H_2O deactivated)	1) Isooctane 2) Benzene	1) Lindane 2) PAHs	– –	F-37
Sewage sludge	Silica gel	1) Hexane 2) Toluene	1) Chlorinated hydrocarbons 2) Pesticides	– –	F-32
Sewage sludge	Silica gel	1) Hexane 2) Methylene chloride in hexane (2:8)	1) Hydrocarbons 2) Aromatics	} 76 to 92%[b]	F-46

See footnotes at end of table.

(Continued)

Table 1 (continued)

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[a] Recovery for column chromatography alone.

[b] Recovery for entire analytical procedure including column cleanup.

F.2.8 Analysis

Analysis of soils sample extracts is usually performed using gas chromatography with either a mass spectrometer or a selective detector. Due to the complexity of the sample extracts, high resolution capillary columns are preferred for compound separation. All of the organics of interest to the synfuels industry should be amenable to GC analysis without chemical derivatization or special column treatments.

Since there are currently no standardized methods for the analysis of soils for the organics of interest and since the matrix effects on any analytical operation will be significant, it is essential that any method selected should be validated prior to use and stringent QA/QC procedures including blank, controls, and surrogate samples be used throughout the analysis program.

F.3 DETERMINATION OF INORGANIC SPECIES

Inorganic species originating from synfuels production find their way into the soil by deposition of airborne particulate material and/or movement by wind and surface water from storage/dump sites. The inorganic species of principal concern in the soil are those which can be released in soluble form. Thus soils are extracted with water adjusted to pH of 5 with acetic acid (F-47). This extract is then analyzed using the same techniques used for water analysis.

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APPENDIX G

GROUNDWATER MONITORING TECHNIQUES

Groundwater supplies the domestic water needs of 80 percent of all public water supply systems and 96 percent of rural America. Overall, about one-half of all U.S. residents rely on groundwater as their primary source of drinking water. Groundwater has traditionally been and continues to be a major source for industrial process water. Moreover, it has come into rapidly increasing use for livestock production and agriculture. Intercepting migrating pollutants before they reach a groundwater supply and detecting their presence and pattern of movement is essential for preventing, reducing, and eliminating deterioration of water supplies.

In identifying the constituents of groundwater which should be monitored, consideration should be given to the groupings of chemicals defined in Appendix C. In making the determination of which chemicals should be monitored, close coordination should be made with the monitoring planned in connection with the source monitoring data base (Section 4.0).

G.1 COLLECTION OF INFORMATION

Shallow aquifers that drain laterally into streams should be monitored for horizontal variations in water quality. Because aquifers generally are not well mixed, more than one well should be placed in a line perpendicular to water flow, and toward the center of the drainage pattern. If vertical variations are suspected, test wells should be constructed at different depths. Sample collection, by pump or other methods, should be preceded by water removal equal to three times the estimated volume of the well to ensure representative sampling. Parameters analyzed should be based on the nature of the potential pollution, and the hydrological and geochemical characteristics of the aquifer. Specific sampling methods will depend on the parameter of concern (e.g., organic compounds require sampling with a peristaltic pump and teflon tubing) (G-1, G-2, and G-3 through G-8).

Existing information and wells could be used, when available, for ambient monitoring. Baseline analysis should include identification and characterization of deep aquifers and interrelationships between different aquifer zones. The ability of soils and the vadose zone to remove pollutants from downward percolating water should be considered. In cases where there is rapid movement through the vadose zone or pollutant potential is high, deep well monitoring is extremely important. At minimum, a single up-gradient well and a series of down-gradient wells should be monitored (G-1, G-2, G-6, G-9, and G-10).

If in-situ gasification is planned for the site, special attention must be given to isolating process waters and treating or removing potential leachates. A series of wells around the zone of activity will be necessary. Monitoring for process-specific pollutants will be necessary. At the present time, options available for treating in-situ wastes are not well known (G-9, and G-11 through G-15).

During the operational phase, suspected pollutant species from plant wastes should be monitored in deep aquifers. This technique is a last line of defense (following surface water and vadose zone interception) in detecting pollutant presence and groundwater contamination from synthetic fuel activities (G-10, G-16).

G.2 FREQUENCY

Monthly samples should be analyzed to establish baseline conditions for all parameters at least one year prior to site activities. During construction and operation, more frequent monitoring may be required if significant changes occur in relative concentrations of existing water quality parameters or if new pollutants are suspected. The monitoring of groundwater should be considered a long term commitment (G-1, G-2, and G-16).

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APPENDIX H

SPECIAL BIOLOGICAL MONITORING TECHNIQUES

H.1 TERRESTRIAL EFFECTS MONITORING

The purpose of terrestrial effects monitoring is to detect potential adverse effects associated with the operation of a synthetic fuel facility. It is not the intent to inventory, measure, characterize, or model the entire ecosystem, including its dynamics, within the local and regional setting of a facility. The emphasis of such monitoring is to observe key species in order to determine if process and emission control systems are effectively controlling the release of pollutants.

H.1.1 Sampling and Analysis

The species selected for observation are routinely examined for residuals of interest and for visible signs of adverse effects at the individual or population level. Examination for both residuals and adverse effects is necessary because several groups of pollutants, although accumulated in the tissues of plants and animals, do not induce visible symptoms. Conversely, several pollutants that cause extensive biotic damage are not accumulated to any appreciable extent. Representative(s) of the first group are metals and hydrocarbons and of the second group is ozone. A third group may accumulate as well as produce visible symptoms (e.g., halogens).

The specific species or biotic groups for study may vary with site specific requirements. Those monitored have included soil decomposers (retarded by chronic exposure to airborne toxic pollutants, e.g., SO_2), fruit flies, earth worms, isopods/millipedes, ants, honeybees, flies, beetles, spiders, starlings, sparrows, house mice, shrews, lichens, mosses, grasses, and various higher plant species (including crops).

There are many important considerations in the establishment of terrestrial monitoring programs focusing on bioaccumulation. These include (in order of priority), importance to the health of man, position of the species in the food chain, importance as an economic resource, species abundance and distribution on and near the site, and collection costs and maintenance. Emphasis should be on the gathering of bioaccumulation data without mortality, especially with respect to important vertebrate organisms (e.g., sampling of blood, hair, feathers).

The general vitality of populations and communities can be monitored by focusing on the observation of changes in numbers of species, species abundance, distribution patterns, diet, longevity, reproductive patterns, and overall diversity. For considerations in the establishment of a site-specific terrestrial monitoring program, the reader is referred to the long-term studies on the bioenvironmental impact of the coal-fired power plant at Colstrip, Montana and to recent documents on terrestrial monitoring protocols (site-specific monitoring: H-1 through H-4; generic observations: H-5, H-6; monitoring protocols and their application: H-7 through H-13).

H.1.2 Frequency

Terrestrial effects monitoring requires a long-term commitment. Continuous monitoring is required, although not dedicated to every species at every point in time. Studies at Colstrip have indicated that certain insects, meadowlarks (pulmonary damage), and Ponderosa pines express symptomatic responses to coal derived pollutants. Such changes, although subtle, are an observable result of long-term monitoring (5 years).

H.2 PERIPHYTON MONITORING

Degradation of water in natural habitats can be detected by monitoring natural communities, especially, with regard to changes in community structure. In the absence of a pollution load, many species are present and most are in relatively moderate abundance. A few species are rare and a few are highly abundant. In the presence of pollution, fewer species are present, they do not occur in the same relative abundances, and a few species are represented by very large numbers.

Data of this nature can be used to indicate stress in an aquatic system, in conjunction with more routine measurements of the physical and chemical parameters. When an abnormal community is observed, chemical testing can be initiated to identify the source and the particular contaminant (H-14 through H-17).

H.2.1 Sampling and Analysis

In-situ monitors such as the Catherwood Diatometer or other artificial substrates can be used to detect the presence of toxic substances, including heavy metals and organic compounds (H-14). Exposure for two weeks or more allows for colonization of the surface. Duplicate surfaces can be analyzed for speciation and for bioaccumulation. Organic compounds may be extracted and analyzed by gas chromatography. A series of substrate colonizations and analyses can indicate fluctuations of pollutant concentrations over time. Placement above and below discharge sites will provide pollutant concentration profiles relative to the facility site. Baseline monitoring can characterize the normal community structure for a particular site. Operational monitoring should consist of at least two stations (above and downstream of the facility) sampled monthly (H-18 through H-21).

H.2.2 Frequency

Monthly samples should be obtained after placing the artificial substrate in the water for a period of at least two weeks in summer to four weeks in winter. Under relatively unpolluted conditions, the kinds of species change from season to season, yet the number of species and community structure are relatively constant. If monthly samples indicate stress in the natural community, then more frequent biological monitoring and monitoring at strategically located sites should be conducted along with chemical analyses to determine the source and extent of contamination (H-14 and H-18).

H.3 AQUATIC BIOACCUMULATION MONITORING

Heavy metals, organic pollutants and radioactive materials tend to accumulate in certain biota at greater levels than in the water column. Potentially hazardous substances may be detected sooner in resident fish, for example, than in ambient water. Because such bioconcentration is known to affect humans, it is important to test for bioaccumulation in the ambient environment around synthetic fuel sites.

H.3.1 Sampling and Analysis

Although bioaccumulation also can be tested in the laboratory through uptake tests, it is presented here as a static measure of ambient water pollutants. Fish may be obtained by active or passive sampling methods, and native species of the same size and age should be collected. In addition, several specimens of representative species should be preserved for future reference and possible analysis. Whole body analysis should be performed by homogenizing several fish within eight hours, and by analyzing tissue and water samples within 48 hours (at least two samples of water should be analyzed for the materials of interest and conventional water parameters) (H-22 and H-23).

Sample analyses should follow standard procedures as described in other sections of this document (in general, atomic absorption spectrophotometric methods for metal, and gas chromatographic methods for organic compounds). No standard method has been developed for this procedure using field samples. However, it is currently used as a fast, efficient method of detecting toxic materials of concern in field monitoring activities (H-24 and H-25).

If the pollutant is being concentrated in fish tissues, tissue measurements should exceed ambient water concentrations (H-26).

H.3.2 Frequency

Annual analyses should be sufficient to detect the presence of toxic materials in the organisms. If significantly high levels are found, then further study of the water body will be necessary to determine the source and extent of contamination and to eliminate hazards to the environment.

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APPENDIX I

SFC INTERIM GUIDELINES

The U.S. Synthetic Fuels Corporation (SFC) has prepared interim Environmental Monitoring Plan Guidelines. These interim guidelines were published in the Federal Register on April 1, 1983, with an invitation for public comments. A copy of the published interim guidelines is attached. Where this Environmental Monitoring Reference Manual refers to the SFC guidelines, it is referring to the published interim guidelines.

In response to public comments received on the interim guidelines, the SFC will be preparing final Environmental Monitoring Plan Guidelines, which will supercede the interim guidelines. The final guidelines will be addressed in any future revision of this Monitoring Manual.

APPENDIX I

SFC GUIDELINES

SYNTHETIC FUELS CORPORATION

Interim Environmental Monitoring Plan Guidelines

AGENCY: U.S. Synthetic Fuels Corporation

ACTION: Publication of interim Environmental Monitoring Guidelines.

SUMMARY: This notice publishes, and invites written public comment on, Environmental Monitoring Plan Guidelines which have been adopted in interim final form by the Board of Directors of the U.S. Synthetic Fuels Corporation to carry out the requirements of Section 131(e) of the Energy Security Act, Pub. L. 96–294, relating to environmental monitoring plans. Written comments will be accepted through May 23, 1983, and should be directed to the Corporation's Director of Environment at the address indicated below. Copies of the Environmental Monitoring Plan Guidelines and all comments thereon will be available in the Corporation's Public Reading Room at the address indicated below. After receipt of comments, the Environmental Monitoring Plan Guidelines will be presented to the Corporation's Board of Directors, with such changes as may be recommended by the Chairman, for adoption in final form.

FOR FURTHER INFORMATION CONTACT: Steven M. Gottlieb, Director of Environment, U.S. Synthetic Fuels Corporation, 2121 K Street, NW., Washington, D.C. 20586, (202) 822–6316.

For copies of the guidelines and public comments: Catherine McMillan, Director of Public Disclosure, U.S. Synthetic Fuels Corporation, 2121 K Street, NW., Washington, D.C. 20586, (202) 822–6460.

United States Synthetic Fuels Corporation, Interim Environmental Monitoring Plan Guidelines

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I. Purpose

Section 131(e) of the Energy Security Act specifies that project sponsors receiving financial assistance from the United States Synthetic Fuels Corporation (the "Corporation") shall develop, in consultation with the Environmental Protection Agency ("EPA"), the Department of Energy ("DOE") and appropriate state agencies an environmental monitoring plan acceptable to the Corporation's Board of Directors. In implementing this statutory mandate, the Corporation is utilizing a two-stage approach under which the sponsors (1) develop an *Outline* of their monitoring plans, which will be incorporated into financial assistance contracts, and (2) develop a monitoring *plan* (based on the outline) after financial assistance contracts are executed.

The purpose of these Guidelines is to set forth the procedural steps to be taken and the broad substantive areas to be addressed in developing outlines and plans. The Guidelines provide the general basis on which the Corporation will determine the "acceptability" of outlines and plans. However, the Guidelines do not specify the substantive details required for an acceptable outline or plan since the actual development of an outline and plan is the responsibility of sponsors, in consultation with the appropriate agencies.

II. Statutory Basis

Section 131(e) of the Energy Security Act ("ESA") requires that:

> Any contract for financial assistance shall require the development of a plan, acceptable to the Board of Directors, for the monitoring of environmental and health-related emissions from the construction and operation of the synthetic fuels project. Such plan shall be developed by the recipient of financial assistance after consultation with the Administrator of the Environmental Protection Agency, the Secretary of Energy, and appropriate state agencies.

The Conference Committee's Joint Explanatory Statement relating to this provision states, in pertinent part:

> The monitoring of emissions—gaseous, liquid or solid—and the examination of waste problems, worker health issues and other research efforts associated with any synthetic fuels project * * * will help to characterize and identify areas of concern and develop an information base for the mitigation of problems associated with the replication of synthetic fuels projects. The Corporation is not expected to involve itself in the development or execution of such plans except for the necessary approval. The conferees intend that development of the plans and actual data collection be reserved to the applicants for financial assistance after consultation with appropriate federal and state agencies. (Joint Explanatory Statement of the Committee of Conference: pp 208–209 of Compilation of the Energy Security Act of 1980.)

III. General Approach To Implementing Section 131(e)

The Corporation views the characterization and identification of areas of concern and the development of an information base for the mitigation of problems associated with the replication of synthetic fuels projects to be the fundamental purposes of environmental monitoring pursuant to monitoring plans under Section 131(e). Toward this end, the Corproation requires that sponsors perform a broad range of monitoring activities, during the entire life-cycle of their project.[1] (Socioeconomic and water consumption monitoring will not be considered to be part of monitoring under Section 131(e); however, it is anticipated that some socioeconomic and water consumption monitoring will be required by separate terms of the financial assistance contract.) Monitoring pursuant to section 131(e) shall include that which is required by federal, state, and local permits, approvals,[2] and other regulatory obligations ("compliance monitoring") and, as appropriate, additional requirements ("supplemental monitoring"), such as the monitoring of unregulated substances which may be present at concentrations of significant environmental or health concern.[3]

The Corporation requires that the environmental monitoring plan be developed in two stages. In the first stage, sponsors are required to develop an outline of the environmental monitoring plan ("outline"), in consultation with the federal and state agencies referred to in section 131(e) (the "consulting agencies"). This outline, which will contain a general description of the sponsors' monitoring tasks, will be incorporated into the financial assistance contracts. Under the second stage, sponsors are required, by a date fixed in the contract, to develop an environmental monitoring plan ("plan") which provides a detailed description, based upon the general terms of the outline, of the specific monitoring tasks to be undertaken. Both the outline and plan shall address the methods by which data will be acquired, managed, and analyzed. The plan should be viewed by sponsors and consulting agencies as a dynamic document which can be modified as conditions warrant.

In determining the "acceptability" of the outline and plan under Section 131(e), the Corporation will decide whether the sponsors have addressed both the broad monitoring areas referred to in the Guidelines and the specific recommendations of the consulting agencies. The Corporation will consider the costs of monitoring relative to the potential usefulness of this information. Where the sponsors do not include in their outlines or plans monitoring which is indicated in these Guidelines or recommended by the consulting agencies, a specific explanation shall be provided which will be evaluated by the Corporation as part of the process of making acceptability determinations.

IV. Procedures for Developing Outlines and Plans

A. General Considerations

To promote the timely development of sound monitoring outlines and plans, with meaningful input from the consulting agencies, the procedural approach set forth below should be used in developing and reviewing monitoring outlines and plans. In implementing these procedures, several general points are relevant:

- Section 131(e) formally designates EPA, DOE and appropriate state agencies[4] as consulting agencies for purposes of developing monitoring plans. While the Corporation has the ultimate statutory responsibility for making acceptability determinations, the Corporation regards the consulting agencies' opinions and comments as fundamental to the development of the outline and plan.[5]
- Early meetings between sponsors and consulting agencies and informal communications between them throughout the process of developing an outline and plan are inherent to the Section 131(e) consultation process. (The Corporation will notify sponsors which consulting agency officials to contact.) Sponsors should bear in mind that they have the responsibility for developing their outline and plan and they should

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[1] "Project" applies to those facilities to be covered by the financial assistance agreement, as well as any dedicated mining operation at the project site which is controlled by the sponsors. "Sponsors" applies to the sponsor or sponsors of a project before the Corporation.

[2] Monitoring required by "approvels" shall include monitoring specified in any federal or state environmental impact statement (EIS) or agency record of decision relating thereto. This in no way implies that the award of financial assistance by the Corporation is a major federal action under Section 102(2)(C) of the National Environmental Policy Act (NEPA). Section 175(b) of the ESA specifically provides that all actions of the Corporation, except for construction and operation of Corporation construction projects, are exempt from the EIS requirements of NEPA.

[3] The Corporation has previously notified sponsors that they must consider the monitoring of unregulated substances. (See, e.g., the Corporation's Second Solicitation Section, Section IV.C.a.1, and Third Solicitation, Section, Section III.B.6.b.2).

[4] The Governor in whose state a project is located designates an "appropriate state agency official" to work with the sponsors to develop the outline and plan.

[5] EPA has prepared a monitoring reference manual for synthetic fuels processes (presently in draft form) which the agency will make available to sponsors to indicate EPA's areas of interest. This manuals contains no requirements; rather, it is a general reference tool which may be used by drafters and reviewers of monitoring plans.

not unduly burden the consulting agencies in this effort.

- A number of sponsors have already begun to develop their monitoring outlines in consultation with the appropriate agencies. In these cases, the Corporation will not require repetition of the procedural steps set forth herein to the extent they have already been effectively performed.
- To maximize coordination among the parties to the process—sponsors, federal and state consulting agencies, and the Corporation—courtesty copies of all formal communications (draft and revised outlines and plans and all correspondence, including consulting agency comments and sponsors' responses) from any party should be provided simultaneously to all other parties.

B. Development of Outlines

The following is the sequence which shall be followed in developing monitoring outlines in consultation with the appropriate agencies:

- For projects submitted under the Corporation's first three general solicitations, sponsors shall initiate preparation of their monitoring outline no later than immediately after passing the Corporation's strength review. For those sponsors submitting proposals under the Corporation's "Competitive Solicitation for Oil Shale Projects" (or comparable solicitations developed in the future), sponsors' technical proposals shall include a schedule for preparing an acceptable monitoring plan outline; the schedule should provide that if the technical proposal is found acceptable by the Corporation, sponsors will immediately initiate preparation of their outline.
- The sponsors' draft outline shall be submitted to the consulting agencies for their review and comment. The sponsors should confer with the Corporation regarding the timing of submission of the draft outline (as well as the revised outline) so that an acceptable outline can be prepared on a schedule consistent with the anticipated financial assistance agreement signing date.
- Consulting agencies should provide written comments to the sponsors on the draft outline expeditiously. It is expected that absent special circumstances, comments will be provided within five weeks of receiving the draft.
- Upon receiving comments from the consulting agencies, the sponsors shall prepare a revised outline which responds to the comments, either by modifying the outline or by explaining (in a cover letter) the specific reasons for not accepting any specific monitoring task suggested by the consulting agencies and for excluding any general monitoring area covered in the Guidelines.
- The revised outline shall be submitted to the consulting agencies for final review.
- Absent special circumstances, the consulting agencies should submit to the Corporation their comments on the revised outline within four weeks of receiving it.
- The Corporation will evaluate the revised outline and the consulting agency comments and determine the outline's acceptability.

C. Development of Plans

Each financial assistance contract will establish a date by which sponsors shall submit their draft and revised plans. It is anticipated that the revised plan will be required approximately four to six months after contract signing, depending on the complexity of the plan and other project-specific circumstances.[6] Following the revised plan's submittal, it must be found acceptable by the Corporation within a time fixed in the contract (approximately two months from the submission deadline).

The sequence for developing a plan, including the time periods for consulting agency comments, is analogous to that for an outline set forth above. In brief, the sponsors develop a draft plan; it will be reviewed and commented on by the consulting agencies; a revised plan will be developed; final comments will be provided by the consulting agencies; and the revised plan and comments thereon will be evaluated by the Corporation and a determination of acceptability is made. Absent unusual circumstances, the plan must be consistent with the terms of the outline. (With respect to modifying the plan during the period in which it is being implemented, see Section VII.B.2.)

D. Determination of Acceptability

The Corporation will determine the acceptability of all monitoring outlines and plans based on whether the sponsors' specific treatment of the broad substantive areas set forth in these Guidelines meets the Corporation's environmental monitoring goals of characterizing and identifying areas of concern and developing an information base for the mitigation of problems associated with the replication of synthetic fuels projects. In making acceptability determinations, the Corporation will evaluate the consulting agencies' comments and monitoring recommendations and the sponsors' responses to the agencies' comments and recommendations.

If the Corporation determines that a monitoring outline is acceptable, it will then be incorporated into the financial assistance contract. As a general rule, if a sponsor's outline is not found to be acceptable, the Corporation will not enter into an agreement for financial assistance until the outline is made acceptable. With respect to monitoring plans, failure to submit an acceptable plan as required by the statute, and failure to properly implement plans determined to be acceptable by the Corporation, will be addressed under the default and remedy provisions of the financial assistance agreement.

V. Substantive Areas of Outlines and Plans

A. Overview

A monitoring *outline* should be a general description of the environmental monitoring tasks which the sponsors will perform, including a summary of compliance monitoring obligations and a brief description of supplemental monitoring tasks. (Where a permit has not yet been obtained, sponsors should include in the outline and plan anticipated requirements based on the terms of comparable permits.) The outline should state what substances will be monitored (both regulated and unregulated), where the monitoring will take place (such as ambient or workplace), how the monitoring would be performed (such as high volume sampler or personal dosimeter), and the duration. The monitoring *plan* shall include all of the specific terms and conditions of permits and other approvals and the specific monitoring tasks relating to supplemental monitoring. The plan should be a detailed description of the monitoring tasks set forth in the outline, including sampling protocols, monitoring site locations, monitoring frequency, monitoring equipment, analytical methods, etc.[7] The plan shall also state what substances will be monitored; if a more detailed list is available at this stage than when the outline was prepared, such additional detail shall be provided.

When sponors have not identified the specific unregulated substances which may be of significant environmental or health concern, the sponsors shall provide in the outline and plan qualitative assessments of the classes of substances (e.g., phenols, polynuclear aromatic hydrocarbons, organic sulfur compounds), likely to be present and the method(s) by which the specific substances will be identified.

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[6] Where monitoring activities, e.g., baseline or construction monitoring, should be initiated prior to completion of the plan, the outline should indicate when this monitoring should begin.

[7] Sponsors may provide in their outlines details on any or all aspects of environmental monitoring that are at a level of specificity not required in an outline but appropriate for a plan. This is solely at the sponsors' discretion and will not affect the Corporation's acceptability determination regarding the outline.

In both the outline and plan, sponsors shall provide (as appendices or by separate submission) sufficient background information on their project to enable the consulting agencies to meaningfully evaluate the outline and the plan. This information should include an overall process description, a process block flow diagram, design performance of environmental control systems, plot plans and layouts and a detailed site description; it shall also include studies, reports, data, etc., which are used to support statements and decisions by sponsors in the outline and plan.

Neither an outline nor a plan need be in any particular format. Sponsors can tailor the format of their outline and plan according to their own specific project reporting systems, but consideration should be given to the comments of the consulting agencies regarding format.

B. Supplemental Monitoring

"Supplemental monitoring," as used herein, refers to any monitoring that is not required by the terms and conditions of permits and approvals or other regulatory obligations, i.e., compliance monitoring. Supplemental monitoring should be performed by sponsors when it can produce environmental and health data which are relevant to project replication, i.e., data which are relevant to comparable facilites which may be built in the future. The need for, and duration of, supplemental monitoring will be determined on a project-by-project basis, with consideration being given to meeting the following broad goals:

- Characterizing and identifying unregulated substances, such as those trace metals and polynuclear aramatic hydrocarbons (PAHs) which are suspected of causing carcinogenesis, mutagenesis, teratogenesis, reproductive effects, other systemic disorders and environmental effects. [8] In developing their outline and plan, sponsors are encouraged to consider a two-phased approach to identify and characterize unregulated substances. The purpose of the first phase is to monitor until sufficient data have been collected to statistically establish an emissions baseline. The purpose of the second phase is to limit the scope of monitoring in a manner which will provide data on those substances which are of significant environmental or health concern, while reducing monitoring costs.
- Identifying and characterizing regulated substances or performing baseline monitoring when not required pursuant to permits. [9]
- Assessing the health risks associated with occupational exposure by conducting comprehensive medical surveillance programs of workers and establishing worker registries.

In addition, sponsors should consider the following points in developing the supplemental monitoring tasks in their outline and plan:

- The Corporation does not expect supplemental monitoring to include monitoring which is relevant essentially to a specific project as a specific site (e.g., monitoring project impact on the local wildlife population) unless such monitoring has broader applicability to project replication. However, such site-specific monitoring if required by permit would be included as compliance monitoring in the monitoring outline and plan.
- The Corporation does not expect sponsors to perform off-site supplemental monitoring with regard to solid and hazardous wastes shipped to facilities owned by others because the receiver is subject to its own monitoring obligations.
- The Corporation does not expect sponsors to perform supplemental monitoring with regard to wastewater after its discharge to publicly owned treatment facilities (POTWs) because these facilities are subject to the monitoring requirements of their own National Pollutant Discharge Elimination System (NPDES) permits.

C. Substantive Monitoring Areas

1. *General.* Sponsors shall monitor during all stages of a project's life-cycle—pre-construction (baseline), construction, operation and post-operation (shutdown of facility and reclamation of site). [10] In monitoring during each of these stages, three generic areas of environmental monitoring—source, ambient, and health and safety monitoring—shall be performed as appropriate to that stage. Other monitoring, such as ecological monitoring, as well as toxicological testing may also be required on a case-by-case basis. In general, monitoring must be conducted during start-up, shutdown, and upset conditions, as well as during steady-state operation of the project.

2. *Source Monitoring.* Source monitoring refers to the monitoring of air emissions (including fugitive emissions), water effluents and solid wastes as they are released from a project's vent, stacks, pipes, etc., as well as to the efficiency of environmental control systems. [11]

- For air emission source monitoring, sponsors shall monitor for regulated substances, including those under applicable New Source Performance Standards, National Emission Standards for Hazardous Air Pollutants (NESHAPs), etc., as well for unregulated substances (including those adsorbed on particulates) which may be present at concentrations of significant environmental or health concern.
- For water effluent source monitoring, including underground releases and releases into POTWs, sponsors shall monitor for regulated substances including those in NPDES permits or specified by EPA "consent decrees", etc., as well as for unregulated substances which may be present at concentrations of significant environmental or health concern.
- For solid waste monitoring, sponsors shall monitor these wastes pursuant to the requirements of the Resource Conservation and Recovery Act as well as monitor for unregulated substances which may be present at concentrations of significant environmental or health concern. (See Section V.B regarding monitoring of solid and hazardous wastes once they are shipped off-site).

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[8] The Corporation views unregulated substances as including those substances not presently regulated under any law and those which may be regulated under one law but not another. For example, a substance may be regulated under the Occupational Safety and Health Act but not regulated under the Clean Water Act; monitoring for such a substance in the water would be a supplemental monitoring requirement, but in the workplace would be a "compliance monitoring" requirement.

[9] When modeling of emissions indicates that concentrations may fall below those levels for triggering permit-mandated monitoring (notably for prevention of significant deterioration (PSD) review), monitoring to determine the actual level of emissions (vis-a-vis calculated levels) of regulated substances should be performed where necessary to develop a data base relevant to project replication. It is expected that such monitoring would be of short duration.

[10] While compliance monitoring occurs throughout a project's life-cycle, supplemental monitoring is principally applicable during the operation stage.

[11] It is expected that sponsors will monitor the efficiency of environmental control systems for all source monitoring activities; however, sponsors are not expected to provide proprietary operation condition information pursuant to the plan.

3. *Ambient Monitoring.* Ambient monitoring refers to monitoring the unconfined environment—the air, water, and land—in the vicinity of a project. Sponsors shall monitor in the unconfined environment the level of substances found in the facility's emissions and discharges.

- For ambient air monitoring, sponsors shall monitor, as applicable by permit, those regulated pollutants identified in EPA's PSD Regulations and NESHAPs, etc., as well as for unregulated substances which may be present at concentrations of significant environmental or health concern. Monitoring of possible public nuisances, such as odor, should also be considered.
- Where the project will be discharging into surface waters, sponsors shall monitor for regulated water quality parameters (chemical and biological oxygen demand, total suspended solids, etc.), as well as for unregulated substances which may be present at concentrations of significant environmental or health concern.
- Where substances have the potential to impact groundwater, groundwater monitoring shall be conducted to identify contamination from leachates, discharges, or underground injection and shall include monitoring for regulated substances listed under the Safe Drinking Water Act, etc., as well as for unregulated substances which may be present at concentrations of environmental or health concern.
- Where substances have the potential to contaminate the soil, soils shall be monitored for regulated and unregulated substances.

4. *Health and Safety Monitoring.* Health and safety monitoring [12] refers both to monitoring workers' exposure to potentially hazardous in-plant emissions and/or conditions associated with the project and to the development of worker registries. The sponsor shall characterize and identify work-related exposures to specific substances or conditions in the facility during routine work, maintenance, repair and sampling activities throughout construction, operation and decommissioning of the facility.

All sponsors shall develop and maintain worker registries, to encompass collecting and storing information on medical and work histories, physical examinations, and industrial hygiene exposure records. Registries should provide information to be used to determine if impacts identified in groups of workers are related to various substances or conditions with which workers had been in contact at synthetic fuels facilities. What the registries cover will be determined on a case-by-case basis depending on the health concerns associated with the facility. Sponsors shall develop, in consultation with the consulting agencies, formats and protocols for the registries which are acceptable to the Corporation, which shall include the method by which the confidentiality of workers' identity will be protected.

5. *Other Monitoring.* It may be appropriate for sponsors to perform ecological or other monitoring as well as toxicological testing (including biomonitoring) in some situations. Ecological monitoring should be performed where substances from the facility have the potential for impacting terrestrial and aquatic species; however, for the purposes of Section 131(e), such monitoring should be included only if the collection of such data would be needed to characterize and identify areas of concern and develop an information base for the mitigation of problems associated with the replication of synthetic fuels plants.

Although not generally considered as a part of monitoring (since it determines dose-response relationships and relative toxicities of substances rather than measuring concentrations), toxicological testing should be performed where there is potential for significant human exposure to unregulated substances of concern with unknown or uncertain toxicities.[13]

D. Quality Assurance/Quality Control

The outline and plan shall indicate what quality assurance/quality control (QA/QC) measures will be taken to assure that environmental monitoring data produced will be sound. The outline should briefly indicate the sponsors proposed QA/QC program while the plan should establish specific requirements of a comprehensive QA/QC program.[14]

E. Data Management; Reporting Requirements

Sponsors shall develop a data management program that addresses the acquisition, storage, retrieval and analysis of the monitoring data for the life of the project.[15] The framework for the data management program should be indicated in the outline and the details of the program should be fully described in the plan.

Sponsors shall submit to the Corporation monthly, quarterly and annual reports containing summaries of pertinent data related to requirements in the outline and plan. Central to the development of an information base for replication of synthetic fuels projects and to the development of the environmental components of Corporation reports required by the Energy Security Act are the summary and analyses of environmental monitoring data and the highlighting of significant monitoring events, which will be the focus of these reports.

Sponsors shall develop, in consultation with the consulting agencies, the format and contents of the reports, which should be indicated in the plan. Consistent with the protection of confidential information, copies of the reports will be made available by the Corporation to consulting agencies directly and will be available for public review in the Corporation's Public Reading Room.

The following are the minimum elements required to be included in each report:

- Monthly Reports

Monthly reports shall contain significant monitoring information from the preceding month including:

—The identification and amounts of unregulated substances found to be present at concentrations of significant environmental and health concern.

—An indication if there were any significant or material changes to the terms of environmental permits.

—An indication if there were exceedances of permit conditions, including a statement by the sponsors as to whether there were notices of violation from regulatory agencies.

—Copies of all compliance reports sent by sponsors to the regulatory agencies.

- Quarterly Reports.

Quarterly reports shall:

—Contain summaries and analyses (including statistical analyses) of the environmental and health monitoring data for the three immediately preceding months, include a characterization of the unregulated substances of environmental and health concern.

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[12] Health and safety monitoring as used herein includes industrial hygiene monitoring and medical surveillance monitoring.

[13] Sponsors should be aware that EPA could specify toxicologic testing as part of its Premanufacture Notification requirement under the Toxic Substances Control Act (TSCA), and are urged to contact EPA early regarding the applicability of TSCA to their project's products.

[14] Federal guidelines on QA/QC are available from EPA and the National Institute for Occupational Safety and Health. See "Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances," Research Report DHHS (NIOSH) Publication No. 80-133, September, 1980; "Interim Guidelines and Specifications for Preparing QA Project Plans," "EPA Report No. QAMS-005/80," December 29, 1980.

[15] The sponsor shall permanently retain all monitoring records or make them available to the Corporation for archiving.

—Assess the project's permit compliance status.

—Identify and characterize the presence of significant levels of unregulated substances and correlate it to the operating conditions of the facility and environmental control performance.

—Discuss the performance of environmental control systems.

—Identify potential problem areas encountered throughout the quarter, e.g., problems with monitoring techniques/procedures, sampling, quality control, etc. and propose preliminary solutions.

—Recommend modification or deletion of monitoring tasks not yielding useful data, including the basis for the sponsors' recommendation.

- Annual Reports.

Annual reports shall:

—Summarize and analyze the monitoring data previously collected and the monthly, quarterly, and annual reports previously submitted. The summary and analysis shall include characterizations of unregulated substances which have been found in concentrations of significant environmental and health concern, and the identification of trends and patterns in the data, including data available in worker registries.

—Based upon monitoring data and the reports which have been submitted, indicate if there are any actual or potential environmental or health impacts.

—Recommend modification, deletion or addition of monitoring tasks, including the basis for the sponsors' recommendation.

—Indicate whether any of the problem areas identified in the monthly or quarterly reports have been resolved and, if not, what additional measures should be taken. Copies of all annual compliance reports or analyses submitted to regulatory agencies should also be included in the annual report.

VI. Confidential Information

The contents of all monitoring outlines and plans (including drafts and revisions) submitted by sponsors will be publicly available as will all formal written comments of the consulting agencies on the outlines and plans.[16]

It is expected that all monitoring data, data summaries, data analyses, reports, etc., provided to the Corporation by the sponsors will not be proprietary or otherwise confidential business information. Any information which is properly designated by the sponsors as confidential (in accordance with the Corporation's Guidelines on Disclosure and Confidentiality) will not be provided to federal or state agencies except as authorized by law and unless its confidentiality is protected.

Public information requests will be handled in accordance with the Corporation's Guidelines on Disclosure and Confidentiality.

VII. Monitoring Review Committee

A. Membership; Meetings

Each financial assistance contract will establish a Monitoring Review Committee (the "Committee") consisting of representatives of the sponsors, the consulting agencies, and the Corporation. The Corporation representative will act as chairperson for the Committee. The Corporation will convene meetings of each Committee at least once per year.

B. Functions

1. *Data Review.* Each Monitoring Review Committee will assess the sponsors' environmental monitoring data, including the monthly, quarterly and annual reports. The main purpose of data review is to determine if there are any significant findings among the data, e.g., data points of excessively high readings or if there are significant trends or patterns in pollutant releases from the project which could result in significant health or environmental impacts in the future.

2. *Modification of Monitoring Requirements.* Based on the Committee's ongoing review of the monitoring data and the monthly, quarterly, and annual reports, members of the Committee can recommend to the Corporation representative that the sponsors discontinue, modify or add monitoring tasks, substitute new analytical techniques or instrumentation as they are developed, or change the format of the above reports. The Corporation, after consultation with the sponsors, will authorize such changes if appropriate. (Modification of sponsors' monitoring plans by the Corporation shall have no effect on the sponsors' responsibility to monitor under federal, state, and local requirements.) Absent unusual circumstances, the Corporation will not require additional monitoring beyond that supplemental monitoring specified in the plan unless the costs of the additional requirements have been, or are being, offset by the elimination of comparable costs.

Monitoring plans should have flexibility so that when sufficient data have been obtained to establish a definitive baseline or when the monitoring data indicate that certain monitoring tasks are found to be relatively unimportant, they can be reduced or eliminated, and, conversely, when monitoring data suggest that certain tasks take on increasing importance monitoring can be expanded. Thus, if an unregulated substance in the work environment is consistently absent from monitoring data, monitoring for it should be reduced in scope or terminated; conversely, where new data in the scientific literature indicating that a particular substance may be of increased health or environmental concern, monitoring shall be expanded under the limitation set forth above.[17]

VIII. Amendments to Guidelines

Amendments to these Guidelines may be authorized in writing by the Corporation. All sponsors with projects before the Corporation at the time any amendment is made will be notified immediately of such amendment. Copies of these Guidelines, as amended, will be available in the Corporation's Public Reading Room.

Dated: March 29, 1983.

Jimmie R. Bowden,

Executive Vice President, U.S. Synthetic Fuels Corporation.

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[16] Copies of all initial and revised monitoring outlines and plans as well as written consulting agency comments thereon will be available for review in the Corporation's Public Reading Room. Consulting agencies may also wish to make these documents available to the public as they deem appropriate.

[17] Where production, process or pollution control or feedstock changes occur that may reasonably be expected to contribute to affecting the emission of unregulated substances of environmental and health concern, monitoring tasks should be renewed or extended accordingly.